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Studies on the Water Sorption of Wood

Division of Wood Physics, Section I

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Contents

1. Introduction

The space occupied by wood in water vapor consists of three components, wood substance, water, and empty space, and they hold a definite relation among them. Under a definite condition, the wood substance keeps an amount of bound water to form aggregate which is in equilibrium with a definite vapor pressure. This equilibrium pressure is called the moisture pressure of wood —the vapor pressure of bound-water in wood substance— and it is distinct from the vapor pressure in surrounding space. The term of moisture pressure has been used from long years ago in a phenomenalistic sense on materials showing property of water sorption in general[1].

The water sorption of wood is a phenomenon where the moisture pressure (p) of wood and external vapor pressure (P) change to reach an equilibrium between them, and it is dependent on the difference (P-p). The water sorption in broad meaning can be divided into the water sorption in narrow meaning and the water desorption according to positivity and negativity, respectively, of the difference.

To discuss on the water sorption of wood, it is prerequisite to determine, in regard to the moisture content, the basal state of wood or the range of the water sorption. As mentioned above, the moisture pressure is the equilibrated pressure of the vapor present in the empty space near the aggregate, and it likely differs from the pressure by the vapor in surrounding space. Determination of the moisture pressure is considerably difficult, and ordinarily it is expressed by the vapor pressure of the external atmosphere at the equilibrium under definite conditions, or alternatively it is often presented by humidity or the ratio (x) of the vapor pressure against saturated vapor pressure ($x=P/P_0$, where P_0 is saturated vapor pressure) at a given temperature. When the moisture pressure is expressed by humidity, the water sorption range of wood exists between $x=0$ and $x=1$, and correspondingly the moisture content varies from 0% to the amount at the saturation point of fiber. The two extreme states are called as absolutely dry and moisture saturated state. Dealing strictly with

[1] Miyabe, H. : Hygroscopic Properties of Materials (in Japanese) Tokyo, (1944).

the absolutely dry state (moisture content 0%) of wood means to define standard state of the wood substance, and detailed investigation of the moisture saturated state is to compare the saturated vapor pressure and water. In the present article, both terms are used for the purpose of convenience, according to ordinary custom.

To study the water sorption of wood in narrow meaning, namely the phenomenon of the change from the initial state $P>p$ to the final state $P=p$, there are two methods at hand, one to treat the changes as function of time and the other to handle finally reached, equilibrated value of the water sorption. The latter method of study on water sorption equilibrium is more advantageous than the former method on the sorption velocity in being easier in thermodynamic and kinetic treatments. Rowen and Simha[1] have recently studied the thermodynamic aspect of water sorption but with wood and cellulose. Similar studies have been made by Barkas[2] on wood. He has discussed on the water sorption hysterisis and others by applying the theory of osmotic pressure in solution to wood. In one sense, thermodynamic study of water solution of wood needs no consideration on the molecular architecture of wood and the mechanism of sorption, and the fact makes an advantage in ready derivation of sorption equation on determination of the states before and after the water sorption. However, this advantage makes a disadvantage regarding to other features of the studies.

The object of the present studies is to examine the phenomenon of the water sorption equilibrium and through the studies to investigate some features of the fine structure of wood. For these purposes, the adsorption theroies on kinetic theory of gas, whose studies being initiated by Langmuir[3] and developed extensively by Brunauer, Emmet, and Teller,[4] are employed as useful means. However, it should be born in mind in applying these theories in studies on the water sorption of wood that they have been used in dealing with rigid gels.

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1) Rowen, J. W. & Simha, R. : *J. Phys. Colloid Chem.* 53, 921 (1949).
2) Barkas, W. W., in Meredith, R. : "Mechanical Properties of Wood and Paper." Amsterdam, North-Holland Pub. Co. (1953).
3) Arii, K. : The Adsorption of Gases on Solids (in Japanese) Tokyo, Eikasha. (1944).
4) Brunauer, S. : The Adsorption of Gases and Vapours Vol. 1 London, Oxford Univ. Press, (1943).

One of the specific aspects of the water sorption of wood is that it accompanies swelling which is frequently encountered in many kinds of high polymer materials. Swelling is defined by Katz[1] to be enlargement in the dimension and reduction in the cohesion among tissues, keeping visual homogeneity, along with sorption of liquid. The causes of swelling have been explained since many years ago by (1) existence of non-crystalline region and (2) existence of a great deal of hydrophilic groupings or other water sorption sites. The sites mean the sources for occurrence of water sorption. A more detailed discussion on the causes of swelling will constitutes the latter half of the present introduction.

The wood substance is almost composed of cellulose, hemicellulose and lignin, and the oriented area of cellulose makes the crystalline region, while the disoriented area of cellulose and other components occupy the non-crystalline region. Every component carry hydrophilic grouping or the points where are electric moments. Since x-ray investigations have shown that micro-crystals of cellulose are not suffered from the influence of miosture,[2] the water sorption of wood would occur in the non-crystlline region including surface of the cellulose micro-crystals; thus it occurs by collisions of freely moving water molecules at the molecules of the various components in the non-crystalline region.

At these collisions, the arrived molecules would be promptly rejected from the surface of the macromolecules or would stay there for a time, depending on the nature of the colliding molecules and the surface on which the collisions occur. In the latter case, the density of the gas on the surface of the macromolecules becomes larger with time. On the other hand, some proportion of the staying molecules will leave the surfance to be again in surrounding space, and therefore, after a long time the number of the molecules leaving the surface and that of the molecules staying there after collision will equilibrate with each other. Leading to adsorption equation by kinetic theory of gas is based on these rather simple assumptions. To keep gas molecules on the surfance staying, there would be assumed existance of force acting to each other. This force is generally called adsorption force and it is not fundamentally different from the

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[1] Katz, J. R. : *Trans. Farad. Soc.* **29**, 279. (1933).

[2] Hermans, P. H. : Physics and Chemistry of Cellulose Fibers, Amsterdam, Elsevier's Publ. Co. (1949).

forces construction solids or liquids. or from those intermolecular or interatomic forces that work to deviate the actual gases from the law for ideal gas[1].

Adsorption is classified into two according to the adsorption forces working there, the chemical adsorption where chemical valencies are the responsible forces and physically the van der Waal's force. The borderline between them has been said to be the force between ion and dipole[2]. The forces working in the range previously defined are likely those acting among dipoles and it may be due to physical adsorption.

Now, the adsorption sites in water sorption of wood and variety of the adsorption forces will be considered. The three hydroxyl groups in a unit pyranose structure of pure cellulose molecule have different energy states from each other. The remaining two oxygen atoms in the pyranose unit hold residual valency and also can be adsorption sites[3]. In regard to, for example, the hydroxyl group attached on the sixth carbon of glucose unit, which has the highest freedom of movement, it is free in different degrees depending on the relative positions of the vicinal glucose molecules. In considering the idea of multilayer adsorption and the complexity of the components, the water sorption of wood could not rigorously be of merely physical nature and it naturally could include wide range of energy distribution at the adsorption sites from closely chemical adsorption to such close to condensation of free water. According to Nayer[4] and Stamm[5], there appears to exist a relationship between the ability to form hydrogen bond that is relatively weak linkage and the swelling of wood, and this can supply a measure to inspect the energy states. Neale has reported that the adsorption heat of cotton is a constant 15.7 Kcal/mol. below approximately 0.16% of the moisture content.

Previously Sheppard[6] has suggested occurrence of one bonding of water molecule at one adsorption site. Neale has considered, from the above result,

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1) de Boer, J. H. : Thed Dynamical Character of Adsorption London Oxford, Univ. Press. (1953), Advances in Colloid Science Vol. 3 New York Interscience Pub. (1950).
2) Brunauer, S. : *loc. cit.*
3) Enderby, J. A. : *Trans. Farad. Soc.* **51**. 106. (1955).
4) Nayer, A. N. & Hosafeld, R. L. : *J. Am. Chem. Soc.* **71**. 2852 (1949).
5) Stamm, A. J. & Tarkow, H. : *J. Phys. Colloid Chem.* **54**. 745 (1950).
6) Sheppard, S. E. : *Trans. Farad. Soc.* **29**. 77. (1933).

that under low moisture contents one water molecle will combine to two adsorption sites that are suitably located. From model studies on such combination states between molecule and adsorption site, the water sorption of cellulose has been studied in terms of statistical mechanics[1]. These make important contribution in elucidating the mechanism of the water sorption.

When the work by the binding of wood substance and water molecule is larger in relation to the intermolecular aggregation energy that constructs wood substance, there occures loosening of structure at various points of the non-crystalline region to cause swelling, thus decreasing the aggregation force of wood. On assumption that the adsorption energy is uniform, the amount of swelling by water sorption is dependent on the amount of the intermolecular aggregation energy that constructs wood substance. For example, it is expected that the amount of swelling by water sorption in the direction of axis will be larger with larger deviation of the direction of cellulose chains from the fiber axis. Actually it has been ascertained by Stamm[2] that there is a relation between the inclination angle of fibril and elongation or shrinkage of the fiber. It is also known that in comparison to usual woods, reaction wood shows little dimention changes in the direction perpendicular to axis[3]. When the amount of aggregation force of wood tissue is expressed by, for example, modulus of elasticity, the long known fact that modulus of elasticity in wood decreases along with increase of moisture content would be clearly explained[4].

In the present article, Chapter 2 will treat the changes of volume and deformation at water sorption of wood to consider the mechanism of the sorption, and based on the results an adsorption equation will be given in Chapter 3, from which sorption heat and velocity constant will be obtained. Chapter 4 considers the constants used in the equation, and discusses the relation between the fine structure of wood and its water sorption.

2. Swelling by Water Sorption

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1) White, H. & Eyring, H. : *Tex. Res. J.* **17**, 523 (1947).
2) Cockrell, R. A. : *J. Forestry* 876 (1946).
3) Onaka, F. : "Wood Research" No. 1 (1949).
4) Kollmann, F. : Technologie des Holzes und der Werkstoff Bd. I Berlin, Springer-Verlag (1951).

2.1. Deformation by Water Sorption

It is considered what will be the deformation of wood that is constructed sterically by wood substance, water and empty space, on an assumption that uniform deformation occurs in the aggregate at equilibrium state of water sorption, or water and wood substance exist in a solid-solution[1] phase.

In general, the fundamental of deformation is such that every position of the deformation can be experessed by first-order equations as follows :

$$\left.\begin{aligned} x' &= x + a_1 x + a_{12} y + a_{13} z \\ y' &= y + a_{21} x + a_2 y + a_{23} z \\ z' &= z + a_{31} x + a_{32} y + a_3 z \end{aligned}\right\} \tag{2.1}$$

Now, a specical case of deformation is considered :

$$\left.\begin{aligned} x' &= x + a_1 x \\ y' &= y + a_2 y \end{aligned}\right\} \tag{2.2}$$

This represents elongation and shrinkage of a thin plate to two directions perpendicular to each other. If, in Fig. 2.1, $a = (r' - r)/r$, then,

$$a = (1 + a_1)^2 \cos^2 \theta + (1 + a_2)^2 \sin^2 \theta - 1 \tag{2.3}$$

The equations (2.2) are used by Greenhill in his discussion on the deformation of wood. Since the values for a_1 and a_2 are small, the terms of higher order may be neglected to give, instead of equation 2.3,

$$a = a_1 \cos^2 \theta + a_2 \sin^2 \theta \equiv a' \tag{2.4}$$

The difference is represented as : $a' = a = \Delta$.

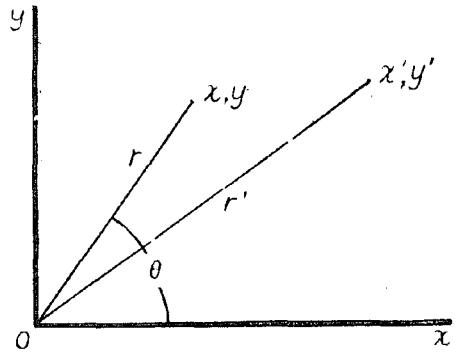

Fig. 2.1.

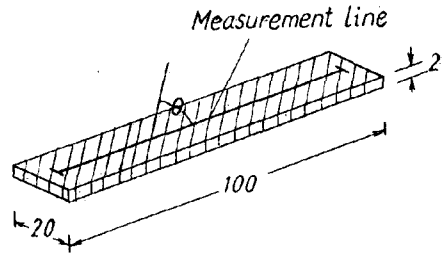

Fig. 2.2

[1] Stamm & Tarkow : *loc. cit.*

Total shrinkage of specimens of Japanese cypress with the dimensions shown in Fig. 2.2 were determined along every direction on the radial surface, against the dimensions in moisture-saturated state, and the results are given in Table 2.1. As found in the table the actual value of α at $\theta=45°$ is 1.71%, and the calculated value using the values for α_1 and α_2 by equation (2.2) is 1.73%, and the corresponding value from equation (2.3) is 1.74%. The maximum value of Δ, therefore, is 0.0001, indicating that it is nearly correct to state $\alpha=\alpha'$. Therefore, the strains along various directions of wood due to moisture absorption are satisfactorily obtained from equation (2.3) when the extent of the strain in the main-axis direction is available.

Table 2.1. Total shrinkage (% against the basal state at moisture-saturation).

θ (degree)	0 (fiber axis)	15	30	45	60	75	90 (radial axis)
maximum value	0.33	0.56	1.80	1.80	2.56	3.10	3.33
minimum value	0.30	0.45	0.94	1.60	2.38	2.87	3.05
average	0.31	0.50	1.01	1.71	2.47	2.98	3.18

Wood will show homogeneous deformation that can be expressed by such a first order equation as given above by setting adequate distance between test points, but if the observation will be extended finer to the level of cellular deformation the changes will be no longer homogeneous as discussed below.

Stamm has determined that the air permeability in wood is constant independently on moisture (accordingly on the moisture content of wood) and has indicated that the dimensions of vacuoles are not varied[1]. These results indicate that deformation of cell membrane will cause no change of the volume of the vacuoles but will contribute directly to the change of the wood dimension.

From the results of Vintila,[2] calculation shows that the ratios of volume shrinkage in summer wood against the one in spring wood are 2.3 in Douglas fir, 2.0 in larch, 1.7 in pine, and 1.7 in fir. Miyabe[3] has obtained with pine the value of moisture density of wood piece under equilibrated moisture-absorption state at 20° and 82% humidity to be 0.107 g./cm.^{3} in spring wood and 0.215 g./

[1] Stamm, A. *J.* : *Physics* 6. 334. (1935).
[2] Vintila, E. : *Holz R. W.* 2. 345. (1939).
[3] Miyabe : *loc. cit.*

cm.^{3} in summer wood. The average value derived from the data of Vintila will agree with the ratio from these values. The data concern only soft wood, but the fact that the ratios on moisture density and on volume shrinkage are nearly equal will suggest that there is a relation between bound water volume and the amount of swelling in wood. Calculation of the ratio of the Raumdichtezahl D in spring and summer wood from the data of Vintila gives a value 2.6 in Douglas fir, 2.5 in lrach, 2.2 in pine, and 2.1 in fir. Stamm[1] has repoted that there is a relation between the number D and the amount of swelling S as follows:

$$S=f\cdot D \tag{2.5}$$

where f is constant corresponding to the fiber saturation points and the ratios in spring and summer wood are 1.2 in Douglas fir, 1.2 in larch, 1.3 in pine and 1.2 in fir. It is now evindent that the ratios of the f values in spring and summer wood are almost constant independently on the species and specific gravity. The values are considered to be a measure for the extent of porosity of the spring and summer wood membranes, and the results will support the data by Ohara[2].

	Staining by Oxaminblau 4R	Porosity
Summer wood tracheid	red	thick
Spring wood tracheid	purplish	rough

Upon the results discussed above on soft wood, the conclusions by Dr. Ohara[2] derived from similar experiments that the tangential membrane is more porous and contains more lignin than the radial membrane will be valid. These data will be helpful in consideration of anisotropic deformation of wood.

The difference in the manner of volume expansion between spring and summer wood will mean expansion of the internal cavity in spring wood and reduction in summer wood. Beiser[3] has confirmed these by microscopic technique

[1] Stamm, A. J. : *Ind. Eng. Chem.* **30**. 1280. (1938).
[2] Ohara, K. : Biological Review (in Japanese) No. 1 (1944).
[3] Stamm, A. J. in Wise & John : "Wood Chemistry" New York, Reinhold, Pub. Co. (1946) Part IV.

on cross sections of spruce and beech.

From the above discussion it is now clear that the volume expansion of wood that contains heterogeneous factors will produce visually homogeneous deformation, and understanding of this will be fundamentally important in approaching the problems.

2.2. Changes in Volume.

Taking for granted that the deformation of wood due to water sorption is homogeneous, the following discussions will be limited on the volume changes. When analyzed volume fraction of wood space at fiber saturation point against the volume of dried wood is given in abscissa and the specific gravity γ_0 of absolutely dry wood in ordinate, there is obtained Fig. 2.3, which has been given by Trendelenburg[1]. In the Fig. 2.3, *ab* represents volume fraction of wood substance, *bc* moisture, *bd* empty space ratio in dried wood, *ce* empty space ratio in moisture-saturated wood, and *dc* amount of swelling.

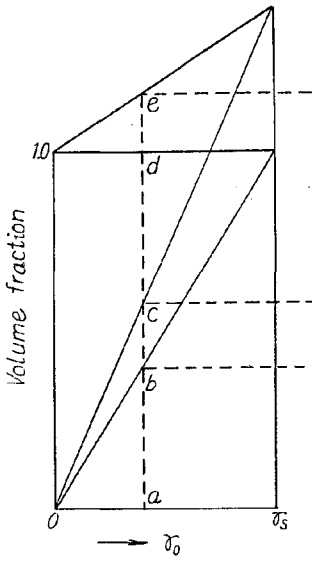

Fig. 2.3.

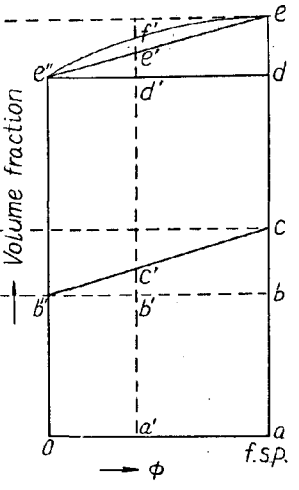

Fig. 2.4

The volume fraction against moisture content ϕ on given γ_0 is presented in Fig. 2.4, where $a'b'$ stands for amount of wood substance, $b'c'$ moisture, $b'd'$ empty space amount under dry state, and $d'f'$ amount of deformation due to

[1] Trendelenburg, R. : *Holz R. W.* 2, 12 (1939).

water sorption.

Now $e''e'e$ is drawn in parallel to $b''c'c$, then

$$d'e'=b'c'$$

and,

$$d'f'=d'e'+e'f'$$

therefore,

$$\delta V=\delta W+e'f',$$

where, $\delta V=d'f'$, $\delta W=d'e'$ (moisture amount).

Dividing both sides by δW,

$$\frac{\delta V}{\delta W}=1+\delta V, \qquad \delta V=\frac{e'f'}{\delta W} \tag{2.6}$$

Meanwhile, it has been reported by many investigators[1] that there exists a reversible relation between δV and ϕ, below about moisture content of 20% as may be represented :

$$\delta V=\beta\cdot\phi, \qquad \beta=\text{constant} \tag{2.7}$$

From the definition of moisture content,

$$\phi=\frac{\delta W}{\gamma_0}$$

therefore the equation (2.6) will be converted into

$$\frac{\delta V}{\delta W}=\frac{\beta}{\gamma_0} \tag{2.8}$$

From equations (2.6) and (2.8).

$$\frac{\beta}{\gamma_0}=1+\delta V. \tag{2.9}$$

The water sorption type of wood is represented as follows :

$$\delta V\gtreqless 0,$$

therefore, it is classified into three typs :

Type I $\delta V>0$, meaning $\beta>\gamma_0$

Type II $\delta V<0$, meaning $\beta<\gamma_0$

Type III $\delta V=0$, meaning $\beta=\gamma_0$

From the measurements by Horioka[2] and Miyabe[3] on 39 representative species, δV is calculated and the relation with γ_0 is presented in Fig. 2.5. Following equation are used for the calculations :

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[1] Stevens, W. C. : *Forestry* 12, 38 (1938).
Miyabe : *loc. cit.*

[2] Horioka, K. : *Bulletin of the Coverment Forest Experiment Station* No. 68. (1954).

[3] Miyabe : *loc. cit.*

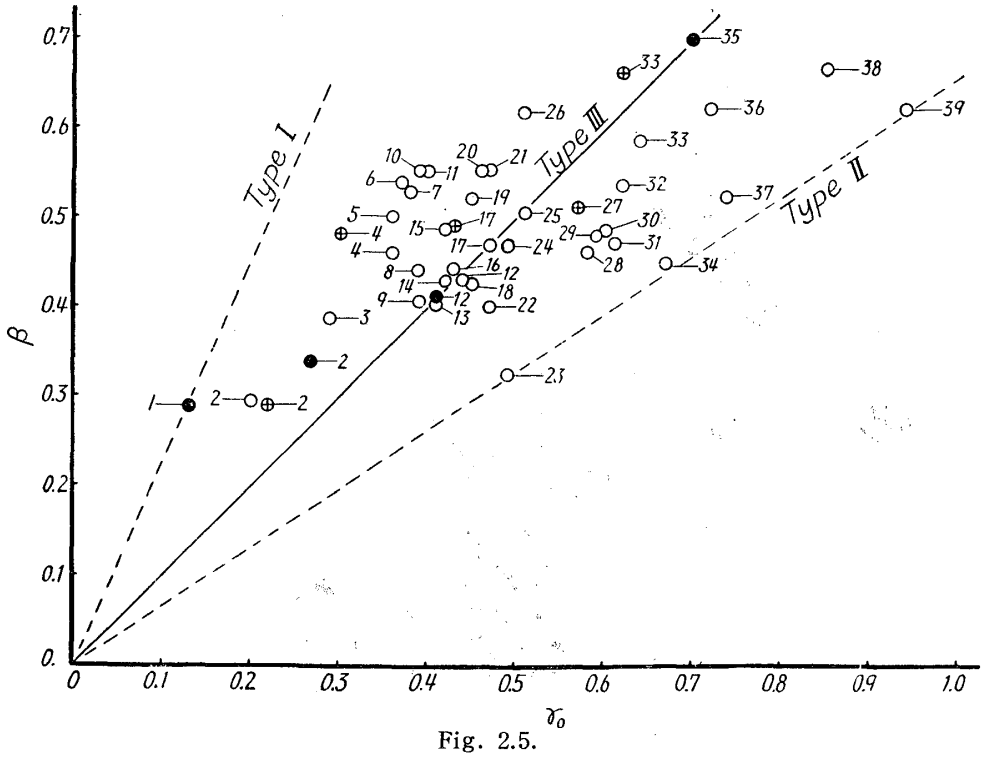

Fig. 2.5.

1. Balsa, Ochroma spp. 2. Paulownia, tomentosa Steude. 3. Sawara, Chamaecyparis pisifera Endlicher. 4. Sugi, Cryptomeria japonica D. Don. 5. Todomatsu, Abies sachalinensis Fr. Schmidt. 6. Shirabe, Abies Veitchii Lindl. 7. Kuromtsu, Pinus Thunbergii Parlatore. 8. Momi, Abies firma S. et Z. 9. Himekomatsu, Pinus pentaphylla Mayr. 10. Doronoki, Populus suaveolens Fischer. 11. Hiba, Thujopsis dolabrata S. et Z. 12. Hinoki, Chamaecyparis obtusa S. et Z. 13. Shinanoki, Tilia japonica Simk. 14. Ezomatsu, Picea jezoensis Carr. 15. Tohi, Picea jezoensis Carr. var. hondoensis Rehder. 16. Akamatsu, Pinus densiflora S. et Z. 17. Katsura, Cercidiphyllum japonicum S. et Z. 18. Taiwanhinoki, Chamaecyparis formosensis Matsum. 19. Onigurumi, Juglans mandsahurica subsp. Sieboldiana (Maxim) Kitam. 20. Harunire, Ulmus Davidiana, var. japonica Nakai. 21. Tsuga, Tsuga Sieboldii Carr. 22. Honoki, Magnolia obovata Thunb. 23. Totinoki, Aesculus turbinata Blume. 24. Harigiri, Kalopanax pictum Nakai. 25. Kusunoki, Cinnamomum Camphora Sieb. 26. Sudazii, Castanopsis cuspidata, var. Sieboldii (Mak.) Nakai. 27. Nara, Quercus serrata Thunb. 28. Keyaki, Zelkowa serrata Makino. 29. Karamatsu, Larix Kaempferi Sarg. 30. Yatidamo, Fraxinus mandshurica Ruprecht. 31. Itayakaede, Acer mono Maxim. 32. Mizunara, Quercus mongolica, var. grosseserrata Rehd. Wils. 33. Buna, Fagus crenata Blume. 34. Makaba, Betula Maximowicziana Regel. 35. Kaede, Acer palmatum Thunb. 36. Tabu, Machilus Thunbergii S. et Z. 37. Mizume, Betula grossa S. et Z. 38. Isunoki, Distylium racemosum S. et Z. 39. Akagasi, Quercus acuta Thunb.

$$\gamma_0=\gamma_{15}\frac{1+0.15\beta}{1.15},\qquad \beta=R+a_T,$$

where, γ_{15} is specific gravity at air-dried state, and a_R and a_T are the amount of deformation due to water sorption per unit moisture content in radial and tangential directions, respectively.

The relation between β and γ_0 obtained from the above data is given in Fig.

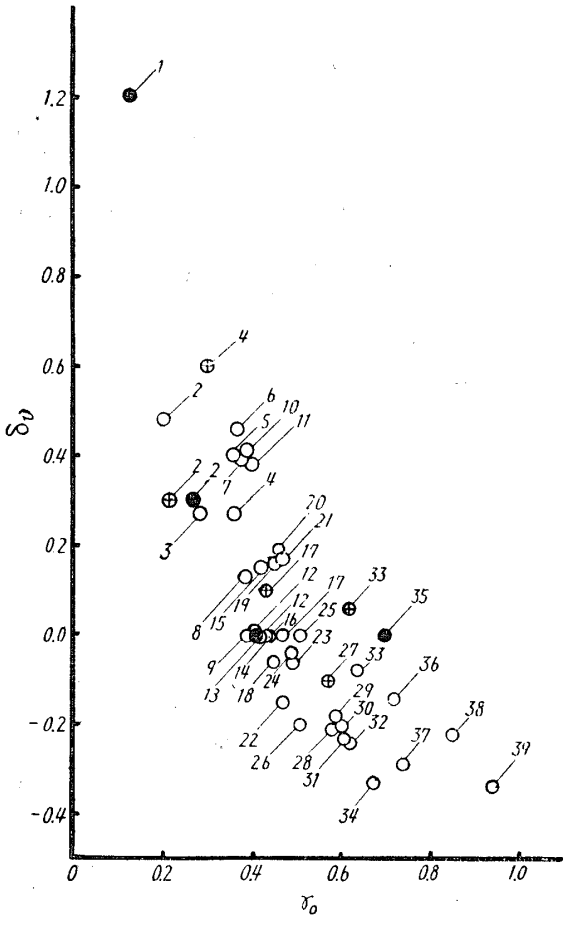

Fig. 2.6.

1. Balsa, ochroma spp. 2. Kiri, Paulownia tomentosa Steudel. 3. Sawara, Chamaecyparis pisifera Endlicher. 4. Sugi, Cryptomeria japonica D. Don. 5. Todomatsu, Abies sachalinensis Fr. Schmidt. 6. Shirabe, Abies Veitchii Lindl. 7. Kuromatsu, Pinus Thunbergii Parlatore. 8. Momi, Abies firma S. et Z. 9. Himekomatsu, Pinus pentaphylla Mayr. 10. Doronoki, Populus suaveolens Fischer. 11. Hiba, Thujopsis dolabrata S. et. Z. 12. Hinoki, Chamaecyparis obtusa S. et. Z. 13. Shinanoki, Tilia japonica Simk. 14. Ezomatsu, Picea jezoensis Carr. 15. Tōhi, Picea jezoeksis Carr. var. hondoensis Rehder. 16. Akamatsu, Pinus densiflora S. et. Z. 17. Katsura, Cercidiphyllum japonicum S. et. Z. 18. Taiwanhinoki, Chamaecyparis formosensis Matsum. 19. Onigurumi, Juglans mandschurica subsp. Sieboldiana (Maxim.) Kitami. 20. Harunire, Ulmus Davidiana Planch. var. japonica Nakai. 21. Tuga, Tsuga Sieboldii Carr. 22. Honoki, Magnolia obovata Thunb. 23. Totinoki, Aesculus turbinata Blume. 24. Harigiri, Kalopanax pictum Nakai. 25. Kusunoki, Cinnamomum Camphora Sieb. 26. Sudazii, Castanopsis cuspidata var. Siebpldii (Mak.) Nakai. 27. Nara, Quercus serrata Thunb. 28. Keyaki, Zelkowa serrata Makino. 29. Karamatsu, Larix Kaempferi Sarg. 30. Yatidamo, Fraxinus mandshurica Ruprecht. 31. Itayakaede, Acer mono Maxim. 32. Mizunara, Quercus mongolica, var. grosseserrata Rehd. et Wils. 33. Buna, Fagus crenata Blume. 34. Makaba, Butula Maximowicziana Regel. 35. Kaede, Acer palmatum Thunb. 36. Tabu, Machilus Thunbergii S. et. Z. 37. Mizume, Betula grossa S. et. Z. 38. Isunoki, Distylium recemosum S. et. Z. 39. Akagasi, Quercus acuta Thunb.

2.6. Keylwerth[1] has given Fig. 2.7 from the data by Morath from which aveage

[1] Keylwerth : *Holz R. W.* 9. 253. (1951).

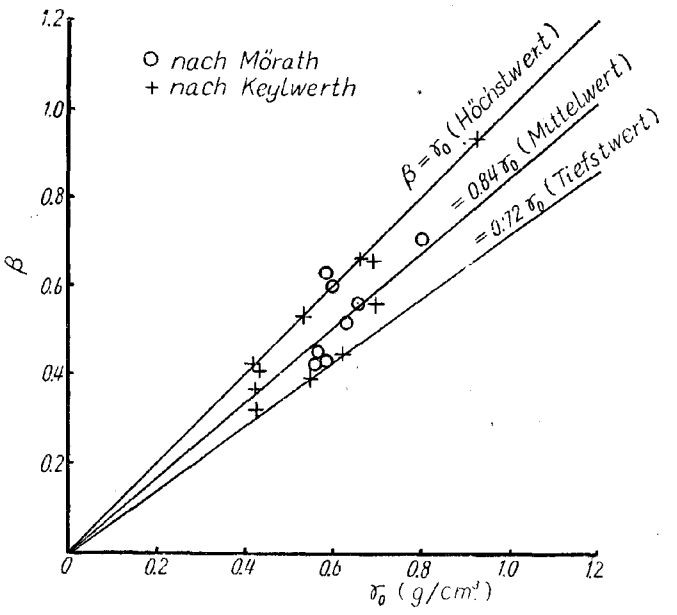

Fig. 2.7. [Keylwerth]

value of δV is calcurated to be -0.16 and belonging to Type II is shown. For the reasons of small amount of swelling for the amount of water sorption, he has given (1) contraction of adsorbed water, (2) swelling of extracted substances, and (3) swelling toward interior of empty space. Considerations will now be given toward these three points.

The decrease of free energy, ΔF, at swelling of wood is consisted of ΔH due to energy effect and $T\Delta S$ due to entropy effect, i.e.,

$$\Delta F = \Delta H + T\Delta S$$

Now it is pressumed that the combination of water molecules and wood substance breaks the combination among the wood substance, and the entropy effect causes augmentation of the distances between the wood substances from each other. In this case, occurrence of loss of energy due to the combination shows clearly contraction in the volume of water, but it has no influence on the changes in external form of wood. It is because that the swelling is due to entropy effect. Stamm[1] has thought that contraction of adsorbed water would influence the swelling of wood and Keylwerth has suggested it as a reason for the Type II water sorption in the present classification, but these may be invali-

[1] Stamm, A. J. in Wise & John. : "Wood Chemistry." New York, Reinhold Pub. Co. (1945) Part IV.

dated by existence of the Type I water sorption. There is also the "empty space" theory by Hermans[1].

It is readily understood that substances that are readily extracted and are precipitated in relatively large vacuoles of cell would not influence on external deformation of wood. Swelling of the tertiary membrance improbably contributes to the external deformation of wood. Meanwhile, the contents of extractable matter and protein in paulownia and balsa, belonging to Type I, were larger than those in oak belonging to Type II[2].

Lastly, swelling toward the interior of empty spaces will be considered. The explanation depends on the definition of the empty space. That the volume of empty spaces that may contribute to permeation of air is independent on moisture content has previously been discussed.

As the fourth factor, contribution of capillary water may be considered, but this will be invalidated later.

As it is obvious from Fig. 2.5, δV will be larger along with smaller γ_0. On the other hand, modulus of elasticity will be smaller as γ_0 becomes smaller. Furthermore, the above discussion will indicate that the reason for various types of water sorption is related to aggregating power of the fibrous molecules in the non-crystalline region.

Japanese cypress and maple belong to the Type III where $e''f'e$ and $e''d'c$ correspond to each other and $e''e'e$ is parallel to $b''c'c$, and therefore,

$$b'c'=d'e', \qquad b'd'=c'd'.$$

This means that in whole range of moisture content, (i) there is no change in the volume of empty space and (ii) the volume of absorbed moisture is equal to the amount of swelling.

To analyze further it is set as follows:

δW_1 : the volume of adsorbed water that contributes to swelling

δW_2 : the volume of adsorbed water that has no relation with swelling

δV : the difference between the amount of swelling and δW_1.

To make $\delta V=0$, there must be satisfied one of the following two equations.

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1) Hermann, P. H. : *loc. cit.*

2) Nishita, K. : Chemical-wooddindustry (in Japanese) Tokyo, Asakura (1947).

$$(1) \quad \delta V = W_2$$

$$(2) \quad \delta V = 0, \qquad \delta W_2 = 0.$$

δW_2 is considered to be the volume occupied by capillary water, multilayer adsorbed water, or both togerther on which discussions will be given in detail.

Mostly the water sorption isotherm with cellulosic matter form S-shapes, and some investigators have regarded those moisture adsorbed in the area above the turning point as capillary water by the reasons (1) that the water sorption occurs even in cellulose triacetate and cellulose trinitrate, (2) of rough calculation of the hydroxyl group number on the micelle, (3) of solubility, and of electric properties. Against these evidences, the first reason is invalidated by recognizing the glycosidic bonding and the remaing one oxygen atom as the site of adsorption, the second by probable occurrence of the site of adsorption in the non-crystalline region, and the third and fourth are disproved by variety of the heat of adsorption.

The evidences disproving the existence of such capillary water[1] are (1) that S-shaped isotherms are obtained even in such a case where capillary condensation is improbable as with water sorption of sulfuric acid, (2) that dimension expansion continues until around the fiber saturation point (capillary-condensed water rather works to reduce dimension of wood), and (3) that the heat swelling is observed in high temperature also. Magne *et al.*[2] from studies on the heat of water sorption of rayon have assigned combined water for below 25% moisture content, co-existence of combined and free water for 25~35% moisture content, and capillary water for above 35% moisture content. Kurosaki has examined the form factors in the theoretical treating of conductivity on water sorption in paper and indicated that capillary condensation does not occur even at 80% humidity[3]. Barkas[4] soaked vacuum-dried specimens of wood into cane sugar solution and estimated the amount of water sorption to find the minumum value of molecular sorption water in sitka spruce as 23%, which is now considered a

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1) Okada, H. : Fundamental Cellulose Chemistry (in Japanese) Tokyo, Shibundo (1946).
2) Ott et. al. : Cellulose and its Derivatives Part 1. New York Interscience Pub. (1954) Chap. IV.
3) Kurosaki : Bull. *Chem. Soc. Japan* 72, 688 (1951).
4) Barkas, W. W. : *Proc. Phys. Soc.* 49, 237 (1937).

reasonable value as a measure.

The existence of multilayer adsorption water is a problem. Multilayer adsorption is a purely physical adsorption whereas the adsorption of molecules relating to swelling is close to chemical adsorption, which is dependent on the rheological properties of wood and so the moisture adsorption velocity is smaller. For the investigation, experiments to compare the amount of water sorption and of dimension expansion as function and of dimension as function of time are required.

The experiments were conducted with test plates of Japanese cypress with

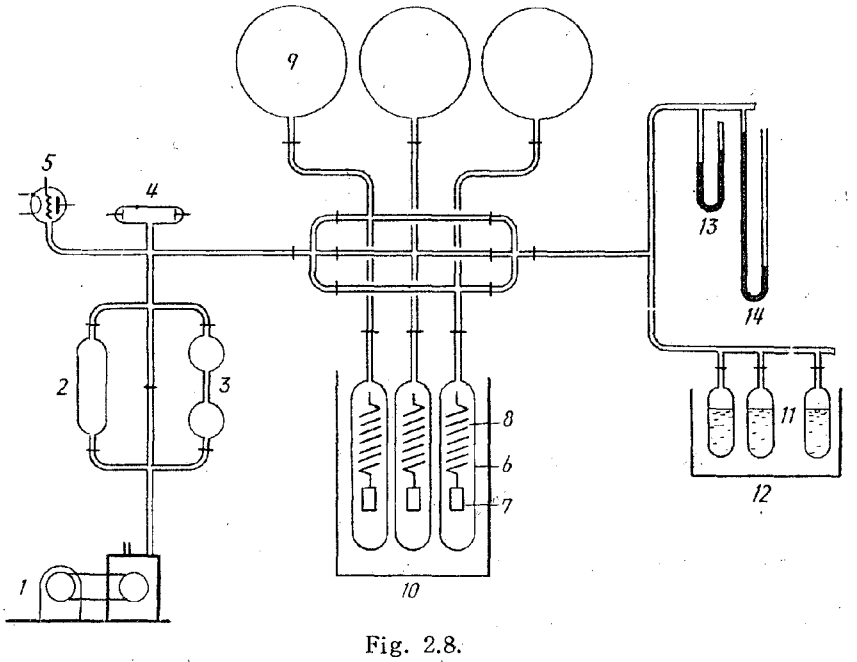

Fig. 2.8.

1. Oil vacuum pump. 2. Oil diffusion pump. 4. Geisler tube.
5. Ionization gauge. 7. Sample. 10, 12. Water bath
13. Closed-end manometer. 14. Open-end manometer.

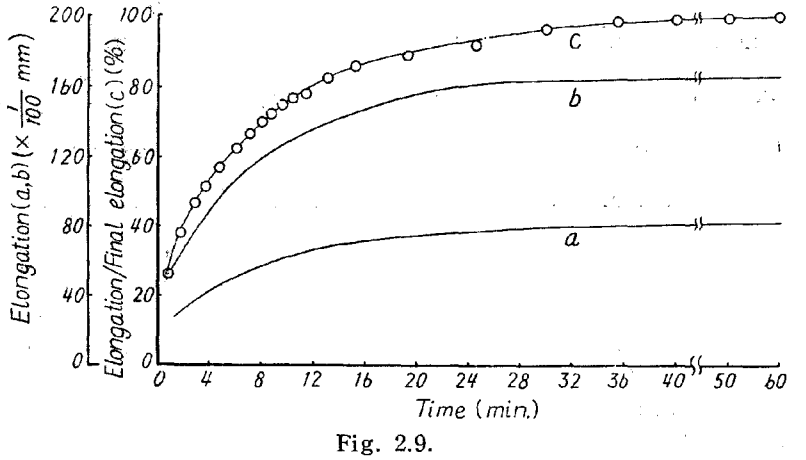

Fig. 2.9.

dimension, 70 mm. in radial direction, 20 mm. in tangential direction, and 1.8 mm. in fiber direction, and with an apparatus shown in Fig. 2.8, and some of the results are given in Fig. 2.9. The sample plates were vacuum-dried at 10^{-3} mmHg to reach basal dry state and water vapor was passed from vapor generator (11) through the adsorption tube (6), and the amount of water sorption was determined by the extent of elongation of the quartz spring (8) and the elongation along the radial direction was measured visually under a microscope to the order of 0.001 cm. There was a linear relation between the load on the quartz spring and the extent of elonagation, and the elongation due to a load of 100 mg. was 4.57 mm.

Now the experimental results can be represented by the following equation:

$$\frac{\delta W}{\delta W\infty}=\frac{\delta V}{\delta V\infty},$$

where δW is the amount of moisture adsorption during time t, δV the amount of expansion, $\delta W\infty$ equilibrated amount of water sorption, and $\delta V\infty$ equilibrated amount of expansion. In Japanese cyprss there is a relation, as previously stated, as follows:

$$\delta V\infty=\delta W\infty$$

Therefore $\delta V=\delta W$

From these results,

$$\delta W_2=0$$

and therefore, the following condition is dominant in Japanese cypress:

$$\delta V=0.$$

The experimental results indicate that during the water sorption, water molecules would not, after temporary staying on the internal surface of wood, creep into the capillary or permeate into the interior part. It is also concluded that inactive molecules will not swell wood and will give very small amount of adsorption under ordinary temperatures.

From the above discussions, the mechanism of water sorption in Japanese cypress which represents the standard type (Type III) of water sorption in wood will be explained as follows: Water molecules approach to the point of adsorption on the surface of micelle or in non-crystalline region through gas diffusion, and under adequate conditions of collisions combination takes place which makes

the distance from vicinal sites of adsorption in non-crystalline region larger. The displacement will cause elastical, external deformation from reversible relation between the amount of expansion and moisture content, and the amount of the deformation is equal to the volume of water molecules adsorbed.

3. Isothermal Adsorption Equation

3.1. Existing Theories

Before presentation of the author's adsorption equation which is derived from the model of water sorption of wood as discussed in the preceding chapter, the existing theories on adsorption which concern the present object will be reviewed and how far these general theories on adsorption could explain the water sorption of wood will be considered.

The equilibrated amount of water sorption ϕ is determined by the final humidity x and temperature T, i. e., $\phi=F(x, T)$. If T is constant, then we obtain

$$\phi=f(x) \tag{3.1}$$

This equation is called isothermal adsorption equation. There are also other adsorption equations, one isobar in which x is kept constant and the other isoster in which ϕ is kept constant. These two equations are often used in investigation on the heat of adsorption, but in actual leading a series of isothermal curves by varying temperature will also give isobar and isosters, and therefore the theories on adsorption have mainly concern the isotherm.

Brunauer *et al.*[1] have classified the type of isotherm obtained by varying combination of adsorbent and adsorbate into 5 types where the water sorption of wood belongs to Type 2 having S-shape.

As isotherm equation, there are in old time Freundlich's empirical formula, the equation by Patrick which modifies the Freundlich's by supplementing consideration on the mechanism of capillary condensation, and Polanyi's equation which extends consideration to the state of adsorption layer[2]. Recently Barrer *et al.*[3] have obtained an equation by studying the equation of state on adsorp-

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1) Brunaure, S. & Emmett, P. H. & Teller, E. : *J. Am. Chem. Soc.* **60**, 309 (1938).
2) Arii, K. : *loc. cit.*
3) Barrer, R. M. & Robins, A. B. : *Trans. Farad. Soc.* **47**, 773 (1951).

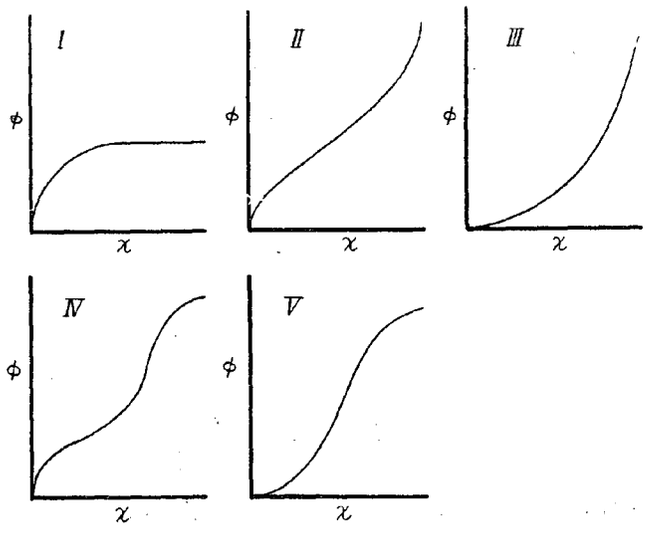

Fig. 3.1. [Brunnauer].

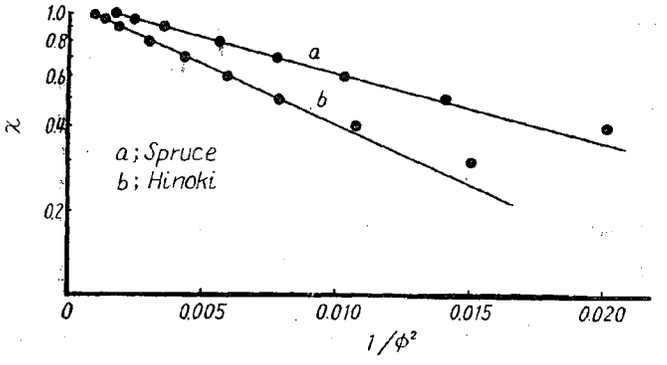

Fig. 3.2.

tion layer. None of these equations is useful in analyzing the sigmoid isotherm.

In the meantime, Jura[1] *et. al.* has applied the Gibbs' two dimensional equation of state to adsorption layer and has derived an adsorption equation, by which x and $1/\phi^2$ are represented by a linear relation. However, in water sorption of wood, this linear relation is held in high pressure region as given in Fig. 3.2, but it is no longer valid in low pressure region. This theory has been often employed to determine the internal surface of catalysts and others.

Boer and Zwikker[2] (1929) have explained adsorption by the induction effect from intermolecular force. Polarity of adsorption sites is induced on the adsorbate and the effect is successively transferred to upper layers resulting in adsorption of gas in multimolecular layer. In the adsorption equation derived

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[1] Jura, G. & Harkins, W. D. : *J. Chem. Phys.* **11**, 430 (1943).
[2] Brunauer : *loc. cit.*

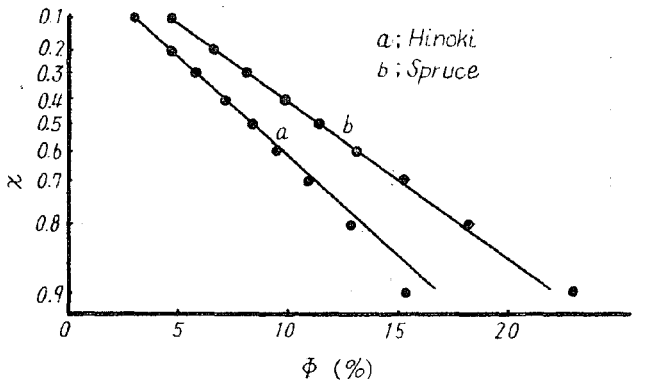

Fig. 3.3.

from these considerations, the relation of log P_0/P against ϕ is linear, where P is vapor pressure and P_0 saturation pressure at a given temperature. When this equation is applied to water sorption of wood linearity is valid only in the medium region of temperature as shown in Fig. 3.3. This equation has been applied to the water sorption of proteins[1].

Deriving an adsorption equation from equilibrium coodition of adsorption from the point of view of kinetic theory of gas has given Langmuir's monomolecular layer theory, and extention of this to multimolecular layer model of such a rigid gel has afforded Brunauer, Emmet, and Teller (B.E.T. theory) and Müttig to establish their theories.

The B.E.T. Theory :

The molecules that are adsorbed on the surface of solid are by themselves become adsorbing sites to adsorb other molecules to form the secondary layer and to lose simultaneously their activity as adsorbing sites. Similarly the molecules in the second layer become by themselves adsorbing sites and form the third layer by adsorbing other molecules. By the similar manner formation of the nth layer occurs under saturated pressure. In a model given in Fig. 3.4,[2]

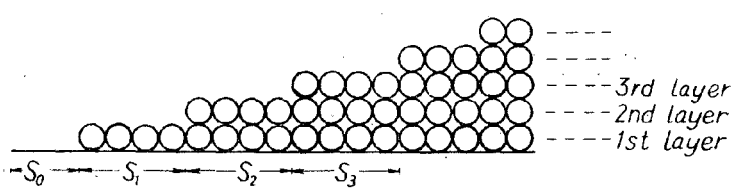

Fig. 3.4.

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[1] Hoover, S. R. & Mellon, E. F. : *J. Am. Chem. Soc.* 72, 2562 (1950).

[2] Miyahara, Y. : *Bull. Chem. Soc.* (*Jap.*) 21, 37 (1948).

S_0 means the surface of the solid and S that of the primary layer on which no second layer is formed.

Brunauer *et al.* has considered the following equilebrium equation for the surface of the solid:

$$a_1 P S_0 = b_1 S_1 P e^{-E_1/RT}$$

where a_1 and b_1 are constants, R gas constant, T absolute temperature, and E_1 the heat of adsorption at adsorbing site; E_1 on all adsorbing sites is presumed to be identical.

For the first layer, similar equilibrium equation is obtained as follows:

$$a_2 P S_1 = b_2 S_2 P e^{-E_2/RT}$$

Where E_2 is the heat of adsorption in the second layer. Similarly the equation for the ith layer is as follows:

$$a_i P S_i = b_{i+1} S_{i+1} e^{-E_i/RT}$$

where a_i and b_i are constants and E_i the heat of adsorption in the ith layer. Now the following assumptions are made:

$$\left.\begin{array}{ll} (1) & a_2/b_2 = a_3/b_3 = \cdots\cdots = a_i/b_i = g \text{ (constant)} \\ (2) & E_2 = E_3 = \cdots\cdots = E_i \cdots = E_L \text{ (heat of liquefaction)} \end{array}\right\} \quad (3.2)$$

and

$$\left.\begin{array}{l} c = \dfrac{a^1}{b^1}\dfrac{b^2}{a^2} \cdot e^{(E_1 - E_2)/RT} \\ x = \dfrac{a^2}{b^2} P e^{E_L/RT} \qquad \text{(relative humidity)} \end{array}\right\} \quad (3.3)$$

then the following equation is derived:

$$\phi = \frac{c\phi_0 x}{1-x} \cdot \frac{1-(n+1)x^n + nx^{n+1}}{1+(c-1)x - cx^{n+1}} \quad (3.4)$$

where ϕ_0 is the amount of adsorption required to cover whole surface of adsorbing body monomolecular. The equation (3.4) is called B.E.T. equation. Babit[1] has applied this equation in analysing the water sorption of cellulose and has found that by taking $n=6-7$ the B.E.T. equation is valid in the range of $x<0.7$. Stamm[2] has calculated the area of the internal surface of wood by using the B.E.T. equation.

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[1] Rowen et. al. : *loc. cit.*

[2] Stamm, A. J. : *TAPPI* 40, 761 (1957).

The constants c and ϕ_0 in the equation (3.4) are obtained by the following equation where $n \to \infty$

$$\frac{x}{\phi(1-x)} = \frac{1}{c\phi_0} + \frac{c-1}{c\phi_0}x \tag{3.5}$$

Examination of this equation on the data of water sorption by Miyabe on Japanese cypress[1] and by Pidgeon[2] on spruce has given results which are shown in Fig. 3.5. In the region of $x > 0.05$, the observed values differ from the theore-

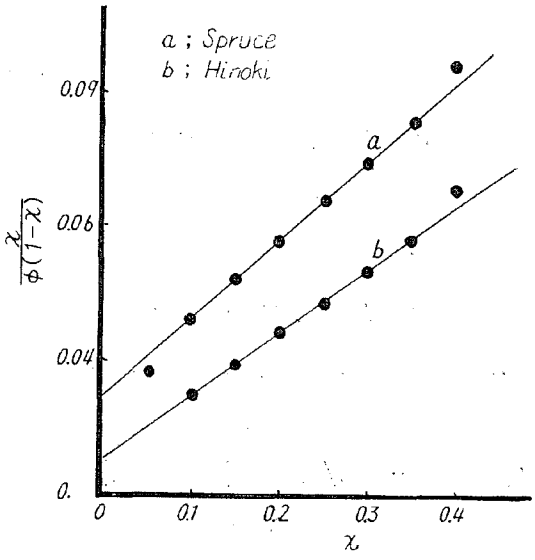

Fig. 3.5.

tical ones. The reason of the difference is, as has been pointed out by Brunauer himself, that in the B.E.T. theory the heat of adsorption on the surface of adsorbate is presumed to be distributed homogeneously while in actual the adsorption energy distribution on the surface is heterogeneous. The multiplicity of the sites of adsorption of wood has been previousle discussed.

Next, high pressure region will be considered. The constants c and ϕ_0 are obtained from Fig. 3.5 and n by trial and error method. Comparison of the isotherm calculated from equation (3.4) and those actually determined is shown in Fig. 3.6 and 3.7 in which discrepancy in the high pressure region is evident. From the following equation to where in equation (3.4) $\phi/\phi_0 = \theta$ is introduced

$$\theta = \frac{cx}{1-x}\,\frac{1-(n+1)x+ux^{n+1}}{1+(c-1)x-cx^{n+1}} \tag{3.6}$$

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[1] Miyabe : *loc. cit.*

[2] Pidgeon, L. A. & Maass, O. : *J. Am. Chem. Soc.* 52, 1053 (1930).

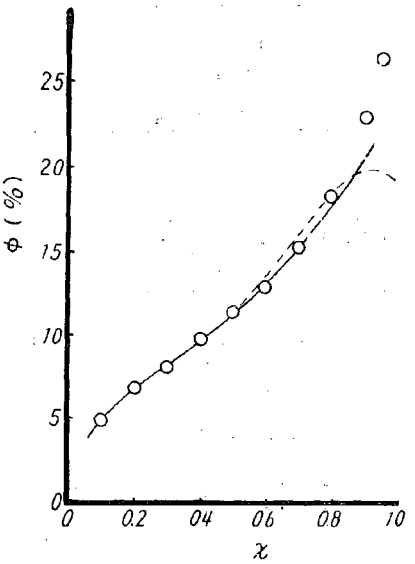

Fig. 3.6.

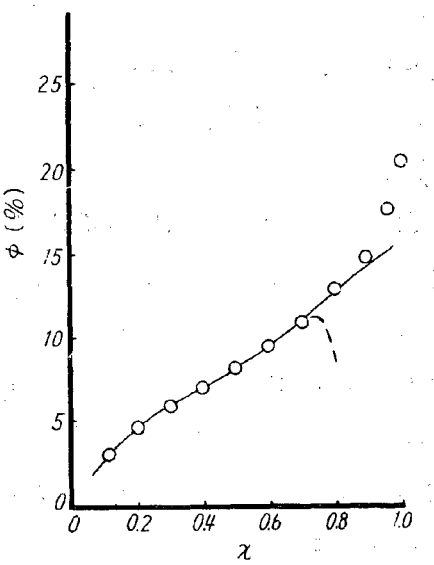

Fig. 3.7

a differential equation for x is obtained

$$\left(\frac{\partial\theta}{\partial x}\right)_T = \frac{c(A+B)}{(1+x)^2(T+(c-1)x-cx^{n+1})^2}$$

In this, an example of $n=5$ and $c=10$ will give the values as shown in the following table.

x	A	B
0.70	3.74	2.78
0.80	1.03	2.20

It is demonstrated therefore that there is a point where a relation $(\partial\theta/\partial x)_T=0$ is satisfied in the range between $x=0.7$ and 0.8. This implies that there must be a miximum in the relation of θ vs x, and the fact makes an important defect of the B.E.T. theory. The above example agrees with the water sorption data on Sitka spruce reported by Pidgeon *et al.* (Fig. 3.7.).

There have been proposed a number of modification and criticism on the B.E.T. theory. Some of the conclusions will be reviewed below.

Pickett[1] has led the following equation on an assumption that the value for b_n/a_n is equal to that of $b_2(1-x)/a_2$

$$\theta=\frac{cx(1-x^n)}{(1-x)(1-x+cx)}$$

where the constants c and n and variable $\theta=\phi/\phi_0$ are identical as in the B.E.T.

[1] Pickett, G. : *J. Am. Chem. Soc.* **69**, 1958 (1945).

theory. For porous adsorbent such as cotton he has introduced in addition constants α and β to give an adsorption equation containing five constants and has demonstrated that by arranging these constants the calculated values can be agreeable with the experimental values; as an example he has given the constants for cotton: $c=11.2$, $n=3.5$, $\phi_0=0.0319$, $a=0.04$, and $\beta=0.85$.

Against this modification by Pickett, Hill has criticized[1] that the assumption on which deriving the equation depends lacks generality and therefore can no longer be basal modification of the B.E.T. theory and that, in addition, involving five constants makes the equation impractical. Barrer *et al.*[2] introduced the following modification of the first of the equation (3.2), the assumption in the B.E.T. theory:

$$\frac{b_2}{m_1 a_2}=\frac{b_3}{m_2 a_3}\cdot=\cdots\cdots\frac{b_i}{m_{i-1}a_i}=\cdots\cdots=g \text{ (constant)}$$

where m_1, m_2,$\cdots\cdots$ are integer or fractional numbers. The general equation thus derived is:

$$\theta=y\alpha\ln\left(1+\frac{cy}{m_1}+\frac{cy_2}{m_1m_2}+\cdots\cdots+\frac{cy_i}{m_1m_2\cdots m_i}+\cdots\cdots\right)$$

where $y=x/g.$, $c=b_1/a_1$.

Whereas Pickett and Barrer have modified the first of assumption in the B.E.T. theory, Anderson[3], Cook[4], and Dole[5] have modified the second assumption. In the Anderson's conclusion, it is obtained for the case of $n\to\infty$ the following equation:

$$\theta=\frac{cKx}{(1-Kjx)(1-Kx+cKx)} \tag{3.8}$$

where, K and j are constants. Against the Anderson's modification Keenan has published a criticism[6]. In adsorption by active carbon, the equation of Anderson is valid to the range of $x=0.7$ excepting the low pressure region in comparison with the experimental values. Cook, on the other hand, has presented an adsorption equation which can agree with experimental values in nearly all

1) Hill, T. L. : *J. Am. Chem. Soc.* **68**, 535 (1946).
2) Barrer, R. M. & Mackenzie, N. & Mcleod, D. : *J. Chem. Soc.* 1952. 1736.
3) Anderson, R. B. : *J. Am. Chem. Soc.* **68**, 686 (1946).
4) Cook, M. A. : *ibid.* **70**, 2925 (1948).
5) Dole, M. : *J. Chem. Phys.* **16**, 25 (1948).
6) Keenan, G. A. : *J. Am. Chem. Soc.* **70**, 3947 (1948).

region, but it is complicated and inconvenient to use in analyzing experimental data.

In the B.E.T. theory, the adsorption energy on the adsorbing surface is assumed to be homogeneous. This has been challenged by McMillan, Halson, Walker and Zettlemoyer. Walker *et al.*[1] have classified the solid surface into two classes according to the height of the adsorbing energy, and combined both by using the simple equation (3.5) for each. This gives a four-constants equation and the determination of constants is considerably difficult. Halsey's conclusion[2] has shown that $\log P_0/P$ vs $\log \theta$ is linear, but the data by Miyabe on Japanese cypress and by Pidgeon on spruce give no linear relation. In the meantime Honig has derived various adsorption energy distribution[3].

In the model given in Fig. 3.4 of the B.E.T. theory consideration is solely paied on the interaction in the vertical direction of the molecules composing adsorption layers. It has been discussed that the interaction in the horizontal direction should be considered also, and general equation has been given for such cases by Hill and Dole[4]. It has also been pointed out that the consideration on the surface tension has to be involved. The relation between the equation by Jura and Harkins which includes the factor of surface pressure and the B.E.T. equation has been reported[5].

Hüttig's theory

In the model shown in Fig. 3.4, the numbers of molecule in respective layers are represented by n_1, n_2, n_3, and so on (the suffix means the number of the layer), and the total number of adsorbed molecules is assigned N. When the number of the molecules required to cover completely the surface of adsorbent is assigned n_0, Hüttig has given the following equilibrium equations for the respective layers, the one for the surfaces of adsorbing body being:

$$a_1P(n_0-n_1)=b_1n_1e^{-E_1/RT}$$

It is obvious from the equation that, while in the B.E.T. theory the evaporation

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1) Walker, W. C. & Zettlmoyer, A. C. : *J. Phys. Colloid Chem.* **52**, 47 (1948).
2) Halsey, G. : *J. Chem. Phys.* **16**, 941 (1948).
3) Honig, J. M. : *J. Phys. Chem.* **57**, 349 (1953).
4) Hill, T. L. : *J. Chem. Phys.* **14**, 441 (1946).
Dole, M. : *ibid* **16**, 25 (1948).
5) Smith, T. D. & Bell, R. : *Nature* **162**, 109 (1943).

of molecules is assumed to be strongly influenced by the molecules laying on them, Hüttig has completely neglected the factor. Applying the idea to upper layers, the following equations are obtained :

$$a_2P(n_1-n_2)=b_2n_2e^{-E_2/RT}$$

$$a_3P(n_2-n_3)=b_3n_3e^{-E_3/RT}$$

.....

$$a_iP(n_{i-1}-n_i)=b_1n_ie^{-E_i/RT}$$

Addition of these equations side by side and treatment as has been done in deriving the B.E.T. equation to determine the constants give the following equation[1].

$$\theta=\frac{cx(1+x)}{1+cx}$$

It is now only needed to examine the linearity of the relation $x(1+x/\phi)$ vs x. In application to the water sorption of wood it gives no linear relation as shown in Fig. 3.8. The reason of this discrepancy will be discussed later.

The Hüttig's equation has been criticized by Hill[2] and by Theimer[3] whose modification is given below :

$$\theta=\frac{cx}{1+cx}\,\frac{1+x-x^s}{1-x^s}$$

If the constant $s=1$, it will be converted into the simple equation of the B.E.T.

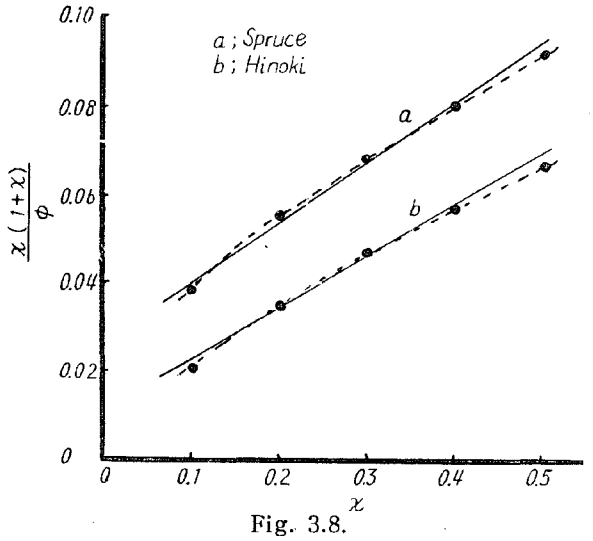

Fig. 3.8.

[1] Ross, S. : *J. Phys. Colloid Chem.* 58, 382 (949).
[2] Hill, T. L. : *J. Am. Chem. Soc.* 72, 5347 (1950).
[3] Theimer, O. : *Trans. Farad. Soc.* 48, 326 (1952).

equation, and if $s=\infty$ it will be the Hüttig's equation.

Recently derivation of the J.H. equation and B.E.T. equation and their extensions have been made by statistical mechanical technique[1], and on the water sorption of fibrous materials there has been published the papers by Enderby[2] and White *et al.*[3] The former has derived an adsorption equation with consideration on swelling in the low pressure region and the latter to that in the high pressure region. The equation by White includes three constants and their determination depends on trial and error method so that it is far from practical convenience. The swelling of a gel and the couse of dissolution have analogy as has been previously reported by Katz. It has formerly been discussed that Rowen *et al.* have presented an adsorption equation through thermodynamic treatment assuming that the energies in the above deformation and in dilution are equal.

3.2. Adsorption Equation

It is obvious from the above discussion that in leading to S-shaped isotherm equations by kinetic theory of gas consideration is invariably dependent on models where multilayer adsorption occur on existing internal surface. The variety of adsorption equations is due to different energy states in regard to adsorbing site and adsorbed molecules and to different conditions under which interactions among the adsorbed molecules take place.

It has been discussed in the preceding chapter that the water sorption of wood is due to monolayer adsorption toward considerably high moisture region. The Langmuir's theory on the monolayer adsorption is inapplicable on the sigmoid adsorption. To overcome the discrepancy, it is recommended to assume that instead of regarding the internal surface as unchanging matter it expands along with proceeding of water sorption. The fashion of the expansion is assumed as described below basing on the conclusion of the preceding chapter.

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[1] Sakai, T. : *Bull. Chem. Soc. (Jap.)* **72**, 62 (1952), **73**, 61 (1953).
Cassie, A. B. D. : *Trans. Farad. Soc.* **41**, 450 (1949).
Miyahara, Y. & Hill & Dole : *loc. cit.*

[2] Enderby : *loc. cit.*

[3] White & Eyring : *loc. cit.*

In Fig. 3.9. the area of the internal surface of wood under basal, dried state is $S(=S_0+S_1)$, and the heat of adsorption on the surface E_1, which, as in the B.E.T. and Hüttig's theories, is assumed to distribute homogenously over the surface. Along with proceeding of water sorption, water molecules are adsorbed in monolayer thereon to occupy the area S_1 remaining $S-S_1=S_0$ as uncovered area. The water molecules that have occupied the area S_1 form the pore by which the water molecules are able to move and newly make the secondary internal surface with area S_1. The heat of adsorption on this new surface is assigned E_2 which is assumed to distribute homogeneously. As the water sorption further proceeds, water molecules are adsorbed in monolayer on this newly formed secondary internal surface to occupy area S_2 and to form the third internal surface S_2 remaining (S_1-S_2) as uncovered surface. In similar manner, under nearly moisture-saturated conditions, the water molecules occupying S_n on the nth surface will form the $(n-1)$th surface with the heat of adsorption E_n, and collision of water molecules on the surface no longer form new surface but make reach an equilibrium. Consideration of the $(n+1)$th internal surface is based on the limited swelling as observed in the water sorption of wood.

On each surface of the model in Fig. 3.9. application of the equilibrium con-

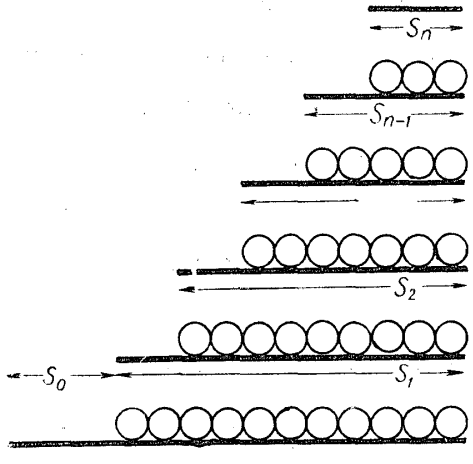

Fig. 3.9.

dition used in the layers in Fig. 3. 4. with consideration of the above features, gives the following equations :

$$a_1PS_0=b_1S_1e^{-E_1/RT}$$

$$a_2P(S_1-S_2)=b_2S_2e^{-E_2/RT}$$

.....

$$a_nP(S_{n-1}-S_n+S_n)=b_nS_ne^{-E_n/RT}$$

Here the hypothetical equation (3.2) and constant (3.3) are employed to give:

$$S_1=cxS_0$$

$$S_2=x(S_1-S_2)$$

.....

$$S_{n-1}=x(S_{n-2}-S_{n-1})$$

$$S_n=xS_{n-1}$$

By adding side by side

$$\sum_{Si}=cxS_0+S_1$$

Now the amount of water required to cover the unit area of the surface in monolayer is assigned u, and that required to cover the primary internal surface (total internal surface of wood under basal dried conditions) in monolayer ϕ_0, then,

$$\phi_0=u(S_0+S_1)=u(1+cx)S_0$$

and the total amount of water sorption is:

$$\phi=u\sum S_i=ucx(1+x)S_0$$

therefore,

$$\theta=\frac{\phi}{\phi_0}=\frac{cx(1+x)}{1+cx} \tag{3.11}$$

The Hüttig's equation (3.9) depends on multilayer adsorption model while in the above equation on expanding surface model, thus differing in the idea, the results are identical. Attention is here directed to that the equation (3.11) that concern equilibrium up to the nth layer does not involves constant n. As will be clarified later, this implied that the equation (3.11) concern extremely special case. It has already been discussed that the water sorption data with Japanese cypress and spruce do not agree with this type of equation.

To assume that $E_1=E_2=E_3=\cdots\cdots E_L$ in expanding surface model means that the primary internal surface differs from the second one in the phase. If the interaction in the vertical direction on the primary surface is neglected but the action is considered on the adsorption on the newly formed internal surface, then the following equilibrium equation are obtained. For each surface the interaction in horizontal direction is neglected.

$$a_1S_0P=b_1S_1e^{-E_1/RT}$$

$$a_2(S_1-S_2)P=b_2(S_2-S_3)e^{-E_n/RT}$$

.....

$$a_nS_{n-1}P=b_nS_ne^{-E_n/RT}$$

Introducing equations (3.2) and (3.3) and treating in a fashion similar to that for above equation (3.11) give :

$$\theta=\frac{cx}{1+cx}\cdot\frac{1-x^n}{1-x} \tag{3.12}$$

The constants c and ϕ_0 are obtained by putting $n\to\infty$ in the above equation as follows :

$$\frac{x}{\phi(1-x)}=\frac{1}{c\phi_0}+\frac{1}{\phi_0}x \tag{3.13}$$

When this equation is supplied to the water sorption of wood, it is represented as in Fig. 3.6 and 3.7. Putting $n=2$ in equation (3.12), we obtain equation (3.9). It is understood therefore that the Hüttig's equation is represented as a special case of the above equation.

Differentiation of equation 3.12 for x gives

$$\left(\frac{\partial\theta}{\partial x}\right)_T=\frac{c}{(1+x)^2(1+cx)^2}[A'-B'] \tag{3.14}$$

$$A'=(1-x^n)(1+cx^2)$$

$$B'=np^n(1-x)(1+cx)$$

To obtain A'/B',

$$\frac{A'}{B'}=\frac{1+x+\cdots\cdots+x^{n-1}}{n}\frac{1}{x^n}\frac{1+cx^2}{1+cx}$$

$$>\frac{1}{x^{(n+1)/2}}\cdot\frac{1+cx^2}{1+cx}$$

therefore

$$\frac{A'}{B'}-1>\frac{1}{x^{(n+1)/2}}\frac{1}{(1+cx)}\{1+cx^2-x^{(n+1)/2}(1+cx)\}$$

$$=(1-x^{(n+1)/2})+cx^2(1-x^{(n+1)/2})$$

If $n\geqq 1$, then $A'/B'>1$.

Actually it is impossible that $n<1$. This makes always $(\partial\theta/\partial x)_T>0$, and therefore it covers the weak point of the B.E.T. theory and that it simplifies the equation for practical use. Also, while in the B.E.T. equation the value of n is

obtained by trial and error method, it is obtained in the equation (3.12) directly for every relative humidity.

The above equation is derived by neglecting the interactions among the vicinal molecules on the internal surface of the same order. The so-called internal surface is an abstracted idea obtained by multiplying the area which is occupied by the adsorbed molecules by the number of the absorbing molecule in monomolecular layer, and it does not imply that there exist continuous planes with such areas. This is easily understood by considering the fine structure of wood. The absorbing sites, therefore, do not exist on surface side by side but they are distributed sterically. These consideration will rationalize to understand the water sorption in wood as non-mobilizable adsorption, except in high pressure region. That the Jura and Harkins' equation which is obtained by applying the two dimensional equation of state on adsorbing layer does not agree, except under high pressure, with the water sorption data in wood will support the above consideration.

The facts that the equation (3.11) which invalidates the interaction among adsorbed molecules does not agree with experimental results and that the equation (3.12) which takes this discrepancy into consideration agrees considerably well with the measured values may suggest that in swelling of wood the energy effect predominates over the entropy effect.

Taking the vertical interactions in Fig. 3.9 on each surface into account as is in the B.E.T. theory, the following equation is obtained :

$$\theta=\frac{cx}{1-x}\cdot\frac{1-x^n}{1+(c-1)x} \tag{3.15}$$

It is interesting that this equation takes identical form as the B.E.T. equation modified by Pickett or Anderson.

According to the expanding surface model in Fig. 3.9, there must be a linear relation between the swelling and the amount of water sorption and the line passes through the original point. It means that there must be a process shown as OaA′ in Fig. 3.10. Actually, however, a process ObB is observed. Such slackening in the volume expansion has been explained by Stamm as due to contraction of the adsorbed water, but, as previously stated, it is the activation energy that is required but not the volume of water. Therefore, it is more

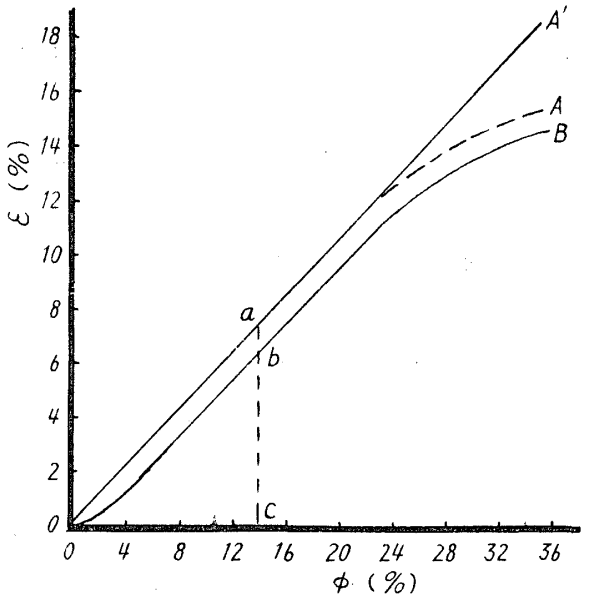

Fig. 3.10.

reasonable to explain it by i) partial filling the empty vacuoles existing in the non-crystalline region, and ii) filling the space between the fibrous molecules (apparent condensation of the adsorbed water). According to Kanamaru[1], the empty vacuoles existing in various fibrous materials occupy 1.1-2.8% the whole amounts, and the value is smaller in such more oriented matter as in ramie and larger in such less oriented one as in straw.

With an assumption that the water applied to fill the empty vacuoles does not participate in the external changes of wood, the Fig. 3.11 is presented. The water molecules that occupy area S_1 on the first internal surface will form the second internal surface K_1S_1. The water molecules occupying S_2 on the second surface will form K_2S_2 on the third surface, and in similar fashion the water molecules that occupy S_n on the nth surface will form K_nS_n on the $(n+1)$th surface. In this model, the equilibrium conditions are considered as follows in the similar way as used to lead equation (3.12).

$$a_1PS_0 = b_1(S_1 - \lambda_2 S_2)e^{-E_1/RT}$$
$$a_2P(KS_1 - S_2) = b_2(S_2 - \lambda_3 S_3)e^{-E_2/RT}$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$a_nP(K_{n-1}S_{n-1} - S_n + K_nS_n) = b_nS_ne^{-E_n/KT}$$

Introducing to these equation (3.2) and (3.3), and the following hypotheses :

[1] Kanamaru, K. and Sobue, H. : The Structure of High Polymers (in Japanese) Tokyo Shukyosha (1948).

$$\left.\begin{aligned} &K_2=K_3=\cdots\cdots=K_n=1 \\ &\lambda_2=0,\ \lambda_3=\lambda_4=\cdots\cdots=\lambda_n=1 \end{aligned}\right\} \tag{3.16}$$

we obtain by the previous method of calculation :

$$\theta=\frac{cx}{1+cx}\left(1+K_1\frac{x-x^n}{1+x}\right) \tag{3.17}$$

when $n\to\infty$,

$$\theta=\frac{cx}{1+cx}\cdot\frac{1-x(1-K_1)}{1-x}$$

or through conversion :

$$\frac{x\{1-x(1-K_1)\}}{\phi(1-x)}=\frac{1}{c\phi_0}+\frac{1}{\phi_0}x \tag{3.18}$$

putting in equation (3.16) $K_1=1$, it is identical with equation (3.12).

K_1 is determined generally in the following way. By comparing Fig. 3.10 and Fig. 3.11 :

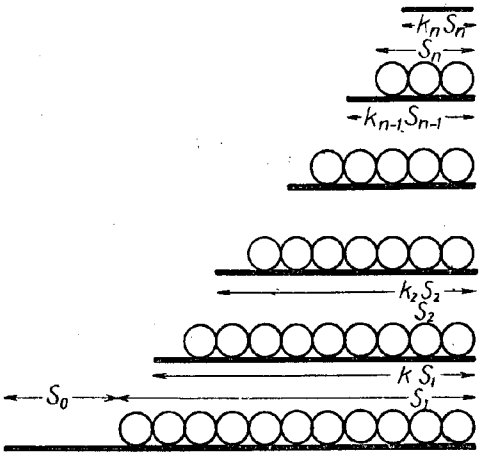

Fig. 3.11.

$$\overline{ab}=uS_1(1-K_1)$$

$$\overline{b0}=u(K_1S_1+S_2+S_3+\cdots\cdots+S_n)$$

$$=uK_1S_1\frac{1-x^n}{1-x}$$

where u is the amount of sorption moisture required to cover the unit area of the surface of absorbent with monomolecular layer. Now if $\overline{ab}\Big/\overline{b0}=\rho$

$$\rho=\frac{1-K_1}{K_1}\cdot\frac{1-x}{1-x^n}$$

and then

$$K_1 = \frac{1-x}{(1-x)+\rho(1-x^n)} \tag{3.19}$$

The relation $\phi-\rho$ calculated from the data in Fig. 3.10 by the method given by Kollmann[1] is represented in Fig. 3.12. For smaller x:

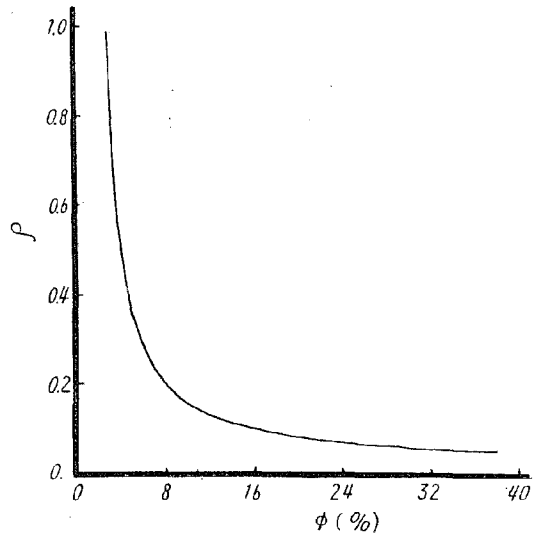

Fig. 3.12.

$$K_1 = \frac{1-x}{1-x+\rho} \tag{3.20}$$

Determination of constants C and ϕ_0 is satiafactorily made by using this approximate value of K_1. Table 3 gives the values of K_1 obtained from the data by Pidgeon *et al*[2] on spruce and those by Miyabe on Japanese cypress. The values calculated with the use of these constants by equation (3.17) and the ex-

Table 3.1.

x	Spruce (23°C)			Japanese cypress (0°C)		
	ϕ (%)	ρ	K_1	ϕ (%)	ρ	K_1
0.1	2.9	0.85	0.51	5.0	0.36	0.71
0.2	4.4	0.44	0.65	6.7	0.25	0.76
0.3	5.7	0.30	0.70	8.1	0.19	0.79
0.4	7.0	0.23	0.72	9.6	0.16	0.79
0.5	8.2	0.19	0.72	11.3	0.13	0.79

[1] Kollmann, F. : *loc. cit.*
[2] Pidgeon & Maass : *loc. cit.*

perimentally determined values reported by them are compared and shown in Fig. 3.13. It is obvious from the figure that they do not agree in high moisture region. This point will be further pursued below.

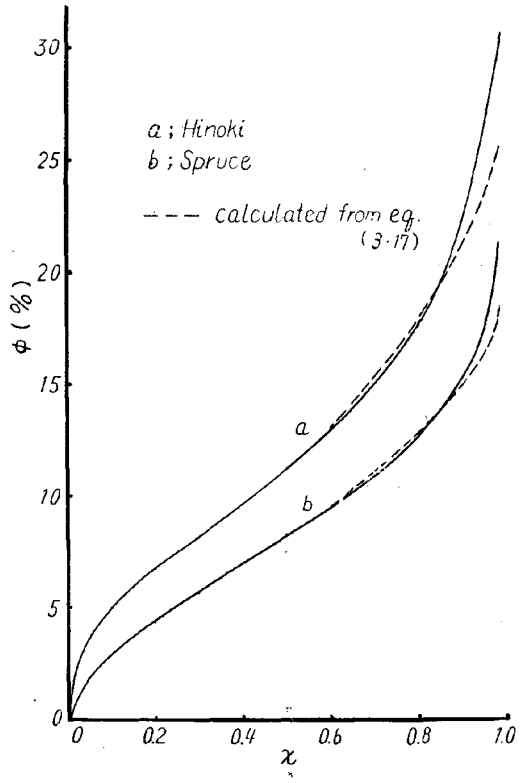

Fig. 3.13.

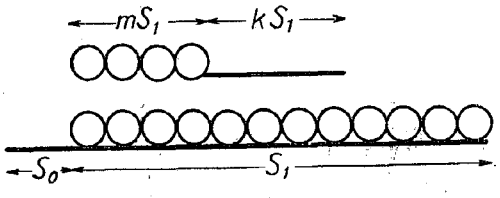

Fig. 3.14.

Table 3.2.

x	Spruce 23°C) n=3.4			Japanese cypress (0°C), n=4.5		
	K_1	m	ϕ(%)	K_1	m	ϕ(%)
0.1	0.51	—	2.9	0.71	—	5.0
0.2	0.65	—	4.4	0.76	—	0.7
0.3	0.70	—	5.7	0.79	—	8.1
0.4	0.72	—	7.0	0.79	—	9.6
0 5	0.73	—	8.2	0.79	—	11.3
0.6	0.73	—	9.5	0.79	—	13.0
0.7	0.74	—	11.0	0.79	—	15.3
0.8	0.74	—	12.8	0.80	—	18.3
0.9	0.75	—	15.2	0.81	0.05	23.0
0.95	0.75	0.1	17.6	0.81	0.12	26.5
0.98	0.78	0.10	20.7	0.82	0.19	30.0

Fig. 3.10 shows that the correlation between the amount of water sorption and moisture content reveals another discrepancy in high pressure region. This appears to be due to the adsorption that accompanies no exqansion of the surface, or to multimolecular layer adsorption to relatively large vacuoles present in the basal dried state of wood. Representation of this phenomenon on the first and the second internal surfaces as model is given in Fig. 3.14, and thenceforth the adsorption equation (3.17) should be modified as follows :

$$\theta=\frac{cx}{1+cx}\left(1+K\frac{x-x^n}{1-x}\right) \tag{3.21}$$

where, $K=K_1+m$; m is a constant concerning the multilayer adsorption in Fig. 3.14. From the data on spruce and Japanese cypress mentioned above, the cal-

Table 3.3.

x	Spruce (23°C) (%)					
	ϕ	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5
0.1	2.9	2.8	0.1	—	—	—
0.2	4.4	3.9	0.5	—	—	—
0.3	5.7	4.4	1.0	0.3	—	—
0.4	7.0	4.7	1.4	0.6	0.3	—
0.5	8.2	5.0	1.8	0.9	0.5	—
0.6	9.5	5.1	2.3	1.3	0.9	—
0.7	10.9	5.3	2.7	1.8	1.2	—
0.8	12.7	5.4	3.1	2.4	1.8	—
0.9	15.3	5.4	3.7	3.3	2.9	—
0.98	20.7	5.5	5.2	5.1	4.9	—
	Japanese cypress (0°C) (%)					
0.1	5.0	4.7	0.3	—	—	—
0.2	6.7	5.6	0.9	0.?	—	—
0.3	8.1	6.0	1.5	0.5	0.1	—
0.4	9.6	6.2	2.1	0.9	0.3	0.1
0.5	11.3	6.4	2.6	1.3	0.7	0.3
0.6	13.0	6.5	3.0	1.0	1.1	0.6
0.7	15.2	6.5	3.5	2.4	1.7	1.1
0.8	18.1	6.6	3.6	2.9	2.3	1.8

culated values are obtained and shown in Table 3.2.

It is obivious from the table that the constant m, and accordingly the multilayer adsorption, appears first in very high pressure region. This fact well corresponds to the conclusion of the preceding chapter on the molecular adsorption water and capillary water.

From the data in Table 3.2, the amount of adsorption on each surface is obtained and given in Table 3.3, where ϕ_1 denotes the moisture content by adsorption on the first internal surface at every temperature and is calculated from $\phi_1 = uS_1$. By similar fashion, ϕ_2, ϕ_3, and so on are obtained.

The Table will clearly demonstrate the manner in which the internal surface expands x. Along with the increase of x, it dose not follow that the adsorption on the first surface is completed and then the adsorption on the second surface starts, but against a given x more or less adsorption take place simultaneously on every surface. Therefore, the relation between the heat of adsorption and moisture content makes no steps but gives a smooth curve as shown in Fig. 3.15. This proves that the hypothesis $E_1 = E_2 = E_3 = \cdots\cdots = E_n$ is reasonable.

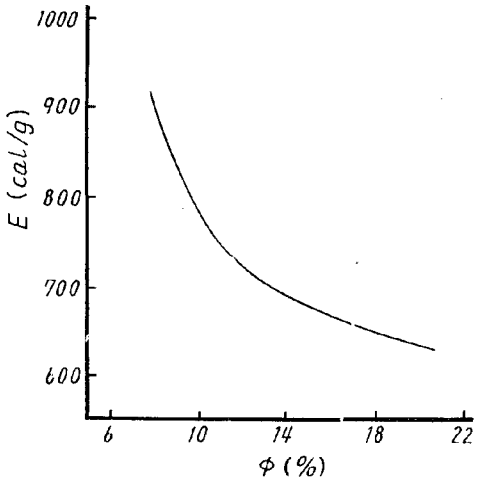

Fig. 3.15.

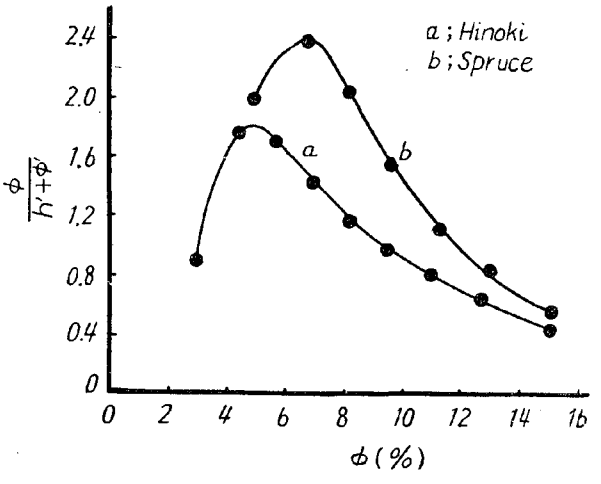

Fig. 3.16.

As is clear from Fig. 3.10, $(1-K_1)\phi_1$ corresponds to the amount of empty spaces filled by water. Putting this h and the maximum value h_{max}, then h_{max} is the volume of the empty space present in the non-crystalline region under dry state. $(h_{max}-h)$ is the empty space which is not yet filled and this is assigned h'. Now the sum of amount of adsorption on all surface above the second is ϕ', and the relation of $\phi_1/h'+\phi'$ vs ϕ can be shown in Fig. 3.16. When this curve is

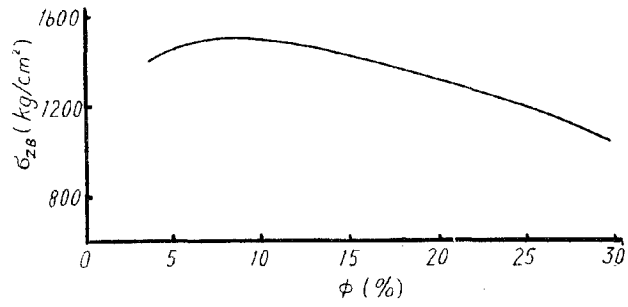

Fig. 3.17. [Kollmann].

compared with the curve in Fig. 3.17 on red beech[1], which shows the influence of moisture content on the tensile strength, it is understood well that the explanation by Hermans[2] on the relation between the tensile strength and moisture content of cotton or on the significance of the dynamic property of ϕ_1 is reasonable. When the water sorption amount of cotton is unity, that of rayon under the identical conditions is 1.9 and wood is 1.25, the fact giving a measure on approximate amount of non-crystalline region. The relation between the tensile strength and moisture content in cotton and rayon are shown in Fig. 3.18[2], and comparison of these and Fig. 3.17 will show that wood reveals behaviors like the one between cotton and rayon.

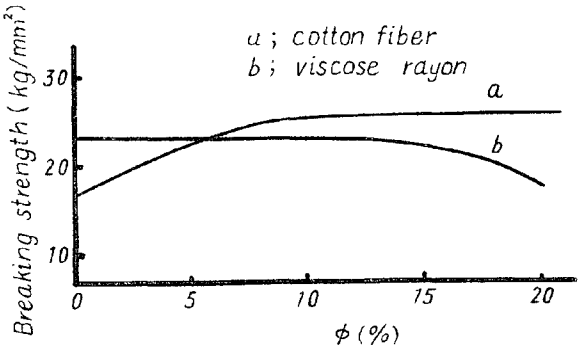

Fig. 3.18. [Hermans].

In leading the equation 3.17, it was assumed $\lambda_2=0$. This implies that the evaporation of water molecules adsorbed on the first internal surface is not influenced by the water molecules adsorbed on the surface above the second. If this influence is taken into consideration, then it is assumed :

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1) Kollmann, F. : *loc. cit.*
2) Hermann, P. H. : *loc. cit.*

$$\lambda_2=\lambda_3=\cdots\cdots=\lambda_n=1$$

and if the other conditions are identical, we obtain the following equation :

$$\theta=\frac{cx}{1+(c-K_1)x}\left(1+K_1\frac{x-x^n}{1-x}\right)$$

3.3. Heat of adsorption

It has been known from decades ago that the isotherm of fibrous materials approaches to the x-axis with increase of temperature, and on wood Stamm *et al*[1] has estimated tha moisture desorption curve with large specimens of spruce and found that the relation between the amount of saturated water sorption and temperature is linear in the range of 25° to 100°, and the inclination is approximately 0.1%. The results on Japanese cypress by Miyabe[2] show the iso-bar to be linear but the inclination is considerably larger than that by Stamm. The data of the water sorption in Japanese cypress with the use of the apparatus for adsorption described in the preceding chapter is given in the accompanying table. Tha temperature is given in °K and the amount of water sorption in %.

x	298°	308°	322°
0.1	3.6	3.3	2.8
0.2	5.0	4.7	4.1
0.3	6.1	5.9	5.3

In general, to calculate the heat of adsorption (E) the Clausius-Clapeyron equation (3.22) is used :

$$E=2.303R\frac{d\log P}{d(1/T)}$$

or by integrating

$$E=4.574\frac{T_1T_2}{T_1-T_2}(\log P_1-\log P_2) \qquad (3.22)$$

where P_1 and P_2 are the vapor pressure at temperature T_1 and T_2, respectively. By this equation the E for $\phi=4\%$ and 5% are obtained from the above data on water sorption and given in the following table ; the unit of E is Kcal/mol.

T_1	T_2	$E_{\phi=4}$	$E_{\phi=5}$
322	308	14.3	13.0
322	298	14.4	13.5
308	298	14.1	14.2

[1] Stamm, A. J. & Loughborough, W. K. : *J. Phys. Chem.* **29**, 121 (1934).
[2] Miyabe, H. : loc. cit.

The net heat of adsorption at 4% moisture content reported to be 150 cal/g. by Stamm *et al.*, and the value at 0% moisture content extrapolation is 270 cal./g. and is closely similar to the above values. Th above values are considerably smaller in comparison to those by Miyabe. Taylor[1] has caluclated on viscose rayon the heat of adsorption as 13.1 Kcal/mol. at $\phi=0.3\%$. Now heat of adsorption obtained by these measurement and that derived from the constant c in the adsorption equation previously described are compared. From the simple equation :

$$\phi=\frac{c\phi_0 x}{1+cx}\cdot\frac{1}{1-x} \tag{3.13'}$$

The constant c and ϕ_0 for the above Japanese cypress sample are tabulated as follows :

T(°K)	c	ϕ_0(%)
298	15.8	5.3
308	14.3	5.0
322	10.4	4.8

On an assumption that ϕ_0 decreases linearly in this range of temperature, it is represented :

$$\phi_0=A+BT$$

and, the net heat of adsorption (E_1-E_L) at $C=Me^{(E_1-E_2)/RT}$ and kinetic factor $M=\frac{a_1}{b_1}\frac{b_2}{a_2}$ is assumed not to be influenced seriously by temperature and equation (3.13') is differentiated for T to give

$$-\left(\frac{\partial\phi}{\partial T}\right)_x=\frac{cx}{(1+cx)^2(1-x)}\left\{\frac{\alpha c_0}{T_2}-B(1+cx)\right\}$$

where

$$\alpha=\frac{E_1-E_2}{R}$$

Rearranging the above equation, α is obtained as follows :

$$\alpha=T^2(1+cx)\left(\frac{\partial\phi}{\partial T}\cdot\frac{1}{\phi}+\frac{B}{\phi_0}\right) \tag{3.24}$$

From this equation, the net heat of adsorption (E_1-E_L) in Japanese cypress is calculated and given in Table 3.4.

---

[1] Taylor : *J. Tex. Inst.* 43, 515 (1952).

Tablee 3.4.

T(°K)	x	ϕ(%)	$E_1-E_L\left(\frac{\text{Kcal}}{\text{mol}}\right)$
298	0.1	3.6	4.0
〃	0.2	5.0	3.9
〃	0.3	6.1	3.8
308	0.1	3.3	4.2
〃	0.2	4.7	4.1
〃	0.3	5.9	3.9
322	0.1	2.8	4.7
〃	0.2	4.1	4.0
〃	0.3	5.3	3.8

A simple equation containing constant K_1

$$\phi=\frac{c\phi_0 x}{1+cx}\left(1+K_1\frac{x}{1-x}\right) \tag{3.18'}$$

is examined for the heat of adsorption. It is readily understood from Fig. 3.12 that ρ vs ϕ is represented as follows:

$$(\rho+a)(\phi+b)=\eta \tag{3.25}$$

The constants are obtained from the data as $a=0.056$, $b=-1.26$, and $\eta=1.60$. Introduction of equation (3.25) to equation (3.20), conversion of K_1 into the function of ϕ, and then introduction of it into equation (3.18′) give:

$$\phi=\frac{c\phi_0 x}{1+cx}\,\frac{(\phi+b)(1-a)+\eta}{(\phi+b)(1-a-x)+\eta} \tag{3.26}$$

This is expressed as before in an approximate form as follows:

$$\phi_0=A+BT$$

Differentiation of equation (3.26) for T gives

$$\frac{\partial\phi}{\partial T}=\phi\left[\frac{1}{c}\frac{\partial c}{\partial T}+\frac{1}{\phi_0}\frac{\partial\phi_0}{\partial T}+\frac{1}{(b+\phi)(1-a)+\eta}\frac{\partial\{(b+\phi)(1-a)+n\}}{\partial T}\right.$$
$$\left.-\frac{1}{1+cx}\frac{\partial(1+cx)}{\partial T}+\frac{1}{(b+\phi)(1-a-x)+\eta}\frac{\partial\{(b+\phi)(1-a-x)+n\}}{\partial T}\right]$$

Introducing to this

$$\frac{\partial\phi_0}{\partial T}=B,\qquad \frac{\partial c}{\partial T}=c\left(-\frac{a}{T^2}\right)$$

and arranging will give

$$a=\frac{E_1-E_2}{R}$$

$$=T^2(1+cx)\left[-\frac{\partial\phi}{\partial T}\left\{\frac{1}{\phi}+\left(\frac{1-a-x}{(b+\phi)(1-a-x)+\eta}-\frac{1-a}{(b+\phi)(1-a)+\eta}\right)\right\}+\frac{B}{\phi_0}\right]$$

The difference of this equation from equation (3.24) is that the former contains the term

$$\left(\frac{1-a-x}{(b+\phi)(1-a-x)+\eta}-\frac{1-a}{(b+\phi)(1-a)+\eta}\right)$$

while the latter does not. But calculation of this term with the values obtained above shows that the value is almost negligible for $1/\phi$. Therefore the following equation can be satifactorily employed for the calculation of the net heat of adsorption.

$$E_1-E_L=RT^2(1+cx)\left[-\frac{\partial\phi}{\partial T}\cdot\frac{1}{\phi}+\frac{B}{\phi_0}\right]$$

It is concluded that the value of the heat of adsorption obtained from calculation by the Clausius-Clapeyron equation and that derived from the constant c in the author's adsorption equation are nearly identical.

3.4. Kinetic Factor

As stated before frequently, the constant c in the adsorption equation is obtained as follows:

$$c=Me^{(E_1-E_L)/RT}$$

(E_1-E_L) is the net heat of adsorption as considered in the preceding section, R gas constant, and T temperature. M is the kinetic factor and is given by condensation coefficients a_1 and a_2 and evaporation coefficient b_1 and b_2 on the first internal surface and the higher surface, respectively.

$$M=\frac{a_1}{b_1}\cdot\frac{b_2}{a_2}$$

In the multimolecular layer model, a_1 and a_2, and b_1 and b_2 stand, each respectively, for the condensation coefficients and evaporation coefficients in the first and higher layer, and E_1 is the heat of adsorption in the first layer.

There are a number of studies concerning M in the multimolecular layer models. Brunauer[1] has regarded $M\fallingdotseq 1$ from the property of a_1, b_1 and so on, while Davis has reported that adsorption of butane on glass gives $M\fallingdotseq 0.7-1.2$;

[1] Brunauer : *loc. cit.*

the latter value is close to that given by Brunauer. However, Gregg has demonstrated that, as given in abstract form in the following table, the net heat of adsorption $(E_1-E_L)_{B.E.T.}$ calculated by the B.E.T. method with $M \fallingdotseq 1$ considerably differs from the experimental value $(E_1-E_L)_{exp}$ and has claimed that the value of M varies depending on condition. Kemball *et al.*[1] have given a wide range of value $M=10^{-5}-10$. Hill has considered theoretically on M in symmetrical biatomic molecules[2] and given the values 2-20 for hydrogen iodide and benzene and some other compounds[3]. Cassie[4] has given the value 1/50 for argon

	$(E_1-E_L)_{B.E.T.}$(Cal/mol)	$(E_1-E_L)_{exp}$(Cal/mol)
Silica gel $-SO_2$	1380	2350
〃 $-H_2O$	700	900
Activated Al $-H_2O$	1450	150

and Beebe[5] has confirmed this result from the adsorption of N_2 on charcoal; Kington[6] has obtained a value with 10^{-3} order. It is important to know how much the value of M is in the water sorption of wood.

Kemball[7] has examined in multimolecular layer model the conditions which fit $M=1$. This idea is now employed to the expanding surface model of the present author and the value of M in water sorption of wood will be pursued.

The equilibrium condition at free liquid surface is given as follows:

$$1=\frac{a_2}{b_2}P_0e^{E_L/RT}$$

where P_0 is the saturated pressure at temperature T. The equilibrium condition on the primary surface is given:

$$a_1PS_0=b_1S_1e^{E_1/RT}$$

Multiplying side to side and arranging will give

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1) Kemball, C. et. al. : *J. Am. Chem. Soc.* 72, 5905 (1950).
2) Hill, T. L. : *J. Chem. Phys.* 16, 181 (1948).
3) Hill, T. L. : *J. Chem. Phys.* 17, 772 (1949).
4) Cassie, A. B. D. : *Trans. Farad. Soc.* 41, 450 (1945).
5) Beede, et al : *J. Am. Chem. Soc.* 69, 95 (1947).
6) Kington, G. L. & Aston, J. G. : *J. Am. Chem. Soc.* 73, 1934 (1951).
7) Kemball, C. & Schreiner, G. D. L. : *J. Am. Chem. Soc.* 72 5609 (1950).

$$P=\frac{a_2}{a_1}\frac{b_1}{b_2}\frac{S_1}{S_0}P_0e^{(E_L-E_1)/RT}$$

Now the vapor pressure at $S_1=S_0$ is P', and then

$$P'=\frac{a_2}{a_1}\frac{b_1}{b_2}P_0e^{(E_L-E_1)/RT}$$

The free energy change of adsorption is known :

$$\Delta G_A=RT\ln P'$$

Substitution of P' in the above equation into this will give :

$$\Delta G_A=-E_1+T\left(\frac{E_L}{T}+R\ln P_0+R\ln\frac{a_2}{a_1}\cdot\frac{b_1}{b_2}\right)$$

It is also well known that the free energy change during liquefaction is given by the following equation with ΔS_L as the entropy change of liquefaction.

$$\Delta G_L=-E_L-T\Delta S_L$$

Therefore,

$$\Delta G_A=-E_1-T(\Delta S_L+R\ln M)$$

ΔG_A is obtained from adsorption energy E_1 and adsorption entropy ΔS_A, and accordingly,

$$\Delta S_A=\Delta S_L+R\ln M \tag{3.28}$$

According to the data by Pidgeon on Sitka spruce, the moisture content required to cover the primary surface (S_0+S_1) (Fig. 3.11) is as previously described (cf. Table 3.3), 5.5%, and therefore the moisture content corresponding to the condition $S_0=S_1$ is about 2.7%, where the adsorption on the higher surface is nearly negligible, as obvious from Table 3.3. Meantime, Stamm *et al.* has given the relation between the amount of water sorption and entropy change as reproduced in Fig. 3.16. With this data, equation (3.28) is calculated to give a value $M\fallingdotseq5\times10^{-2}$.

In such cases as above where the entropy change accompanying adsorption is known, the value of M can be calculated from equation (3.28), but when the entropy change is not known the M value is obtained by measuring several isotherms, calculating the constant c from the adsorption equation, and determining from the following equation the point where the line $\log c$ vs. $1/T$ crosses logarythmic axis :

$$\log c=\log M+\frac{E_1-E_L}{2.303R}\cdot\frac{1}{T}$$

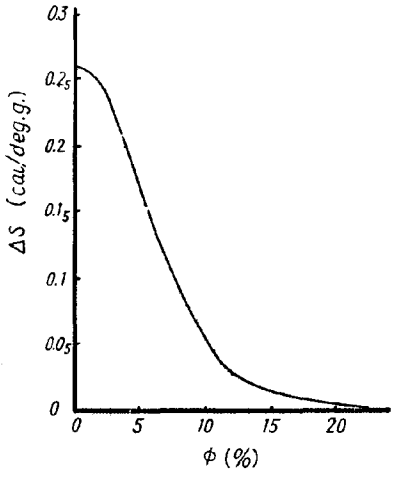

Fig. 3.19. [Stamm & Loughborough].

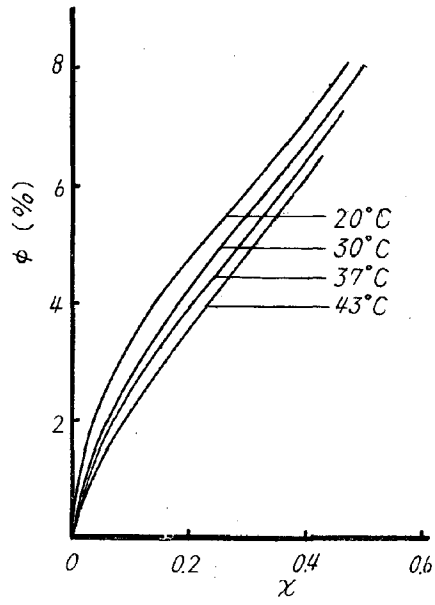

Fig. 3.20.

Application of this latter method to beach wood has given $M \fallingdotseq 0.01$. The experiment was conducted with the apparatus described before and the isothermal curves obtained are given in Fig. 3.20.

4. Internal Surface

4.1. Area of Internal Surface

The area of internal surface has been determined by microscopic technique, by intra-solution adsorption, by wetting heat measurement (these have been applied to wood by Stamm and Millet), by permeation method (applied to fiber by Sullivan), by heat conduction measurement (on catalysts by Jura and Powell), methoxy group determination (on ramie by Harris), and by gas and vapor adsorption method.

As expected from the structure of wood, the internal surface of wood includes the surface of cellular vacuoles, the surface of unoccupied space in the non-crystalline region of dry wood, and the surface newly formed by swelling. Among the above-mentioned methods, Stamm[1] used microscopic method, the method of the adsorption of stearic acid from the benzene solution, the method of inflection point of nitrogen adsorption curve, and the method of permeability of benzene and found that the approximate value of the internal surface in suger pine is $2.2-2.5\times10^3$ cm^2/g. This means that the area of the inner vacuole sur-

[1] Stamm, A. J. & Millet, M. A. : *J. Phys. Chem.* **45**, 43 (1941).

face, and the amount ($\phi(\%)$) of moisture adsorption when water molecules are placed densely in monomolecular layer on this surface is calculated by the following formula :

$$\phi = \frac{A}{\sigma} \frac{M}{N} \times 10^2$$

A : the area of inner vacuole surface

σ : cross-sectional area of water molecules

M : molecular weight

N : Avogadro's number

to give the value, $\phi = 0.007\%$ on $= 10.8$ Å[1]. This gives only the basal dry state in adsorption experiment. This implies that it is the inner surface of cell membrane but not the surface of cellular inner vacuoles that plays important role in moisture sorption of wood. It is therefore significant to consider on the internal surface in detail.

As have been discussed heretofore, the problems in the water sorption of wood are the collisions of water molecules on wood substance molecules which exist in non-crystalline region of cell membrane by weak interaction and subsequent molecular exchange, or under what conditions the water molecules approach to the fibrous molecules and how the orientation varies consequently. The adsorption sites are presumed to consist of internal surface layer and adsorption water layer in macroscopic view, but in microscopic view it does not imply that there is actually a plane with difinite dimension. Those actually exist are adsorption sites on wood substance molecules, which are distributed in the space in the non-crystalline region. The internal surface means, as previously discussed, the amount derived by multiplying the number of water molecules adsorbed on these adsorption sites in monomolecular layer by the cross-sectional area of the adsorbed molecules. This is a useful quantity in theoretical treatment of the adsorption phenomenon.

Stamm[2] has measured the area of the internal surface of wood from the amount of saturated adsorption of polar vapor, adsorption of water from sodium chloride of glycerol solution, and by adsorption heat method using Bartell and

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[1] Livington, K. K. : *J. Colloid Sci.* 4 447 (1949).

[2] Stamm, A. I. & Millett, M. A. : *loc. cit.*

Fu equation. It may be inadequate, however, to apply the adsorption heat method on such porous materials as wood. Brunauer[1] has pointed out that the vapor adsorption method is relatively easier to measure and more useful than any other metheds. According to Stamm[2], the internal surface area of Sitka spruce is 4×10^6 cm²/g., which is calculated on an assumption that the inflection point of isotherm shows the limit of surface-adsorbed water and capillary-condensed water. Existence of the capillary-condensed water has been discussed previously. In the multimolecular layer theory of B. E. T., the internal surface area A is calculated from the constant ϕ_0 in the adsorption equation :

$$A=\frac{\sigma\phi_0 N}{M} \tag{4.1}$$

By this method Stamm has obtained a value of 254 m²/g. for Sitka spruce and 235 m²/g. for sugar maple. To calculate the internal surface area by adsorption theories, the Jura and Harkins' equation and Hüttig's equation are also used. However, it has been discussed in the preceding chapter that these equation are not satisfactory in dealing with the moisture absorption of wood.

The isotherm of Japanese cypress at 16° is given in Fig. 4.1 which was obtained by the apparatus for adsorption experiments previously mentioned.

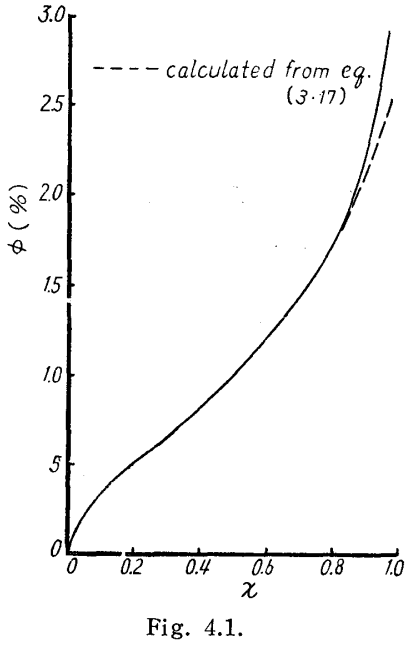

Fig. 4.1.

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[1] Brunauer : *loc. cit.*

[2] Stamm, A. J. : *TAPPI* **40**, 761 (1957).

x	ϕ cal. (%)	ϕ exp. (%)
0.7	13.5	13.5
0.8	16.5	16.5
0.9	20.5	20.6
0.95	22.9	24.5
0.98	24.4	27.8
0.99	25.0	30.5
0.999	25.4	—

Table 4.1.

x(%)	ϕ(%)	θ	K	E(Kcal/mol)
0.046	0.151	0.025	0.56	15.1
0.122	0.300	0.050	0.43	15.1
0.236	0.450	0.075	0.34	14.5
0.38	0.600	0.10	0.29	14.4
0.76	0.904	0.15	0.23	14.0
1.30	1.21	0.20	0.19	13.8
1.94	1.50	0.25	0.17	—
2.64	1.78	0.30	0.16	13.5
3.30	2.04	0.34	0.16	13.2
4.21	2.33	0.39	0.15	13.1

Table 4.2.

x	ϕ(%)	θ	K
0.05	2.36	0.09	2.0
0.2	5.0	0.20	1.25
0.25	5.6	0.22	1.13
0.3	6.2	0.24	1.06
0.35	7.0	0.27	1.07
0.4	7.7	0.30	1.08
0.5	9.4	0.39	1.17
0.7	13.5	0.53	1.6
0.9	20.6	0.81	4.7

Calculation of ϕ_0 value from equation (3.18) gives a value 6.3. Therfore the amount of the primary internal surface in Fig. 3.11 is approximately 230 m^2 per 1 g. wood from equation (4.1). The number of adsorbed water molecules is thus 2.1×10^{21}. The equation (3.17) is converted into the following equation from the above data :

$$n=\frac{1}{\log x}\cdot\log\left\{x-\frac{1-x}{K_1}\left(\frac{1+cx}{cx\theta}-1\right)\right\} \tag{3.17'}$$

From this equation it is obtained $n=5.5$ and therefore the value corresponding to fiber saturation point $n\times\phi_0=34.7\%$. Comparison of the calculated value (ϕ cal) with these constants and the determined value (ϕ exp) in high pressure region is given in the following table.

It is understood that multilayer adsorption occurs in the region of x 0.9. This table also indicates that the amount of moisture sorption (monomolecular adsorption) required to cover total internal surface including high order surface is about 25.5%. The internal surface corresponding to this value is about 930 m^2/g. It show therefore that the internal surface area of 1 g. wood under completely dry state is 230 m^2 and that it increased on moisture saturation to 930 m^2, thus creating new surface of 700 m^2 during the water sorption.

4.2. Distribution of Adsorption Energy

It is obvious from Fig. 3.15 that the adsorption energy at the adsorption sites of wood is not homogenous. Graham has presented a general method to examine the existence of the intermolecular actions among the adsorbed molecules as well as to measure the heterogeniety of the adsorption surface. Now a symbol o stand for the adsorbed molecule, ⊥ for the unoccupied adsorption site and ♀ for the occupied adsorption sites and then the process of adsorption can be expressed as follows :

$$\circ+\perp\rightleftarrows\varphi$$

He has shown that the equilibrium constant K is obtained by the following formula :

$$K=\frac{\theta}{(1-\theta)x} \tag{4.2}$$

where, $\theta=\phi/\phi_0$, and ϕ_0 corresponds to the constant in B. E. T. equation. In an ideal case where the adsorption energy on every adsorption site is identical

and there is no interaction among the adsorbed molecules, the value of K will be a definite one, but, according to Graham[1], along with the deviation from the ideal state the value of K is no longer definite and takes various shapes as shown in Fig. 4.2 depending on the state of the adsorption phase. This theory will be applied below to the water sorption in fibrous materials and the results are compared with those reported by Graham on inorganic material with an intention to examine the validity.

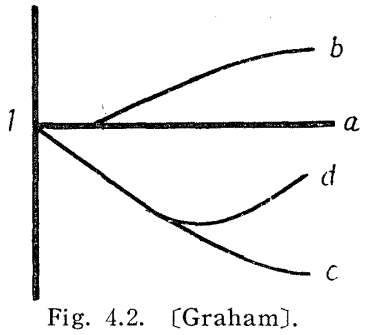

Fig. 4.2. [Graham].
a : ideal. b : uniform-interacting.
c : non-uniform—non-interacting. d : non-uniform—interacting.

The results by Taylor[2] on the estimation of the water sorption in viscose rayon in very low pressure region has indicated that the adsorption equation of Langmuir type is not valid. The reason of this discrepancy has been said, as previously discussed, that, in contradiction to the assumption of the theory, the adsorption energy of the surface of the adsorbing body is not homogeneous. The value of K is calculated by equation (4.2), from the data of Taylor, and the results are shown in Table 4.1, which indicates that the type C in Fig. 4.2 fits to this case. In other word, it proves that the adsorption equation of Langmuir type is not valid for the region with $x<0.05$.

The water sorption of Japanese cypress which was mentioned above in the region of $x>0.05$ is the subject of the next consideration. In equation 4.2, ϕ_0 is used to mean the monolayer capacity in multimolecular layer adsorption model, and when this is applied to the model where the surface expands with a value 25.5% for the monolayer capacity of the Japanese cypress and calculated by equation (4.2), the results as shown in Table 4.2 are obtained. This fits the

[1] Graham, D. : *J. Phys. Chem.* 57, 665 (1653).
[2] Taylor : *J. Tex. Inst.* 43, 515 (1952).

a type in Fig. 4.2, and it is clearly demonstrated that the surface is heterogeneous and there is no interaction among adsorbed water molecules up to ϕ=about 7 %, and above this there occurs and gradually increases the attractions among the adsorbed water molecules to each other. These facts prove the validity of the present author's consideration in the course of derivation of the adsorption equation (equation (3.21)) in the expanding surface model that the evaporation from the first internal surface is free from the interactions of the vicinal molecules while the evaporation from the higher surface accompanies them.

Taylor[1] has reported that the water sorption isotherm of rayon in very low pressure region follow the Freundlich formula :

$$\theta = AP^c \tag{4.4}$$

where A and c are constants. Sips[2] has derived the distribution function of adsorption energy from the Freundlich's equation. From the result, the number N (E) of adsorption site with an adsorption energy E will show the following exponential distribution by the use of equation (4.4) :

$$N(E) = \frac{Aac}{RT} \frac{\sin \pi c}{\pi} e^{-CE/RT}$$

where a is a constant. Reversedly application of the exponential function distribution to $N(E)$ gives equations of the Freundlich type[3]. These will lead us to a conclusion that the adsorption sites contributing to the water sorption of viscose rayon in this region follow exponential function distribution.

Comparison of the constants in the water sorption isotherm and relevant equations on rayon with those on Japanese cypress, or consideration on the heat of adsorption will indicate an analogy in these regards between the two materials. In addition, the constituent of these materials are similar to each other, and therefore it is reasonable to assume that the adsorption sites of Japanese cypress, which concern water sorption in very low pressure region will also follow exponential distribution.

In the region with intermediate pressures, log P is not proportional to log θ. This indicates that the energy distribution on the surface is not exponential.

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1) Taylor : *loc. cit.*
2) Sips, R. : *J. Chem. Phys.* **16**, 490 (1948).
3) Halsey, G. & Taylor, H. S. : *ibid.* **15**, 624 (1947).

If it follows a box-type distribution, then it must be that $\theta \infty \log P$, and $E \infty \theta$. In Japanese cypress these relations are hardly satisfied. Owing to the agreement of the present author's equation, previously given, which involves two kinds of energy E_1 and E_L on surface, and the experimental data in this region, the internal surface of Japanese cypress may be classified into the following three classes.

1) the surface with exponential distribution (x 0.05, $\phi = 2.3\%$)
2) E_1-surface ($\phi = 2.3$-6.3%)
3) E_2-surface ($\phi = 6.3$-25.5%)

4.3. Changes by Heating

It is a well known phenomenon that heat treatment of adsorbent reduces the internal surface and it is called sintering. For example, when coconut charcoal is treated at 900-1000°C the amount of N_2 adsorbed is 8.2 cc./g. at 25° under 760 mmHg while when heated at 1100-1300°C it is 3.9 cc./g. and when at 1600°C 0.2 cc./g[1]. Usually the mechanism of sintering is explained by growth of minute bodies by heating. Heat treatment of fiber materials increases the birefringence as shown in the accompanying table on viscose rayon.

Treatment	Birefringence of viscose rayon
Non-treatment	0.0128
Steam-heating (100°C)	0.0150
Dry-heating (100°C)	0.0154

This means the increase of crystallinity of the material by heating. That heating augments the crystalline region of fiber materials is also proven by X-ray studies[2]. It has slso been reported that the heat treatment increases the heat of adsorption. These factors are examined now on wood and the significance of the constants n and ϕ_0 in equation (3.21) will be discussed in reference to the structure of surface.

On the cnstant n.

The amounts of water sorption at given time of the wood dried by dielec-

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1) Brunauer, S. : *loc. cit.*
2) Kanamaru, K. & Sobue, H. : The Structure of High Polymers (in Japanese) Tokyo, Shukyosha (1948).

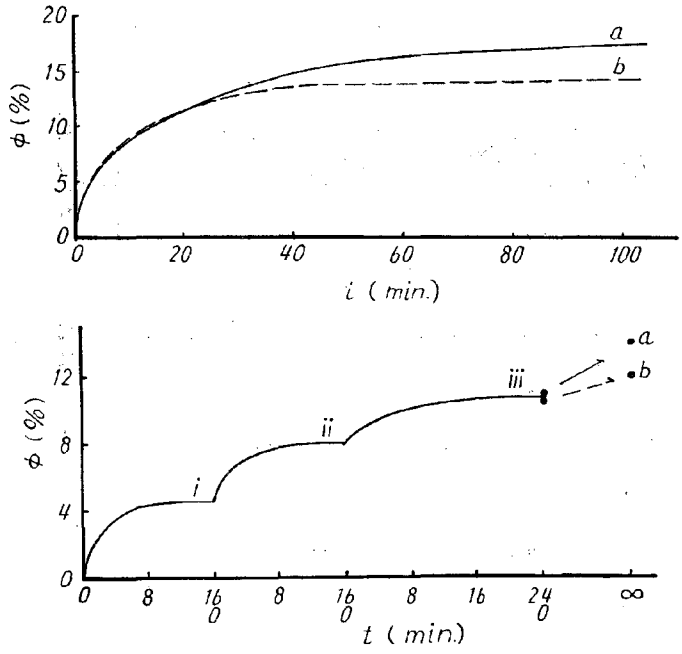


Fig. 4.3.
a : spontaneously dried specimen. b : specimen dried by dieledtric heating.

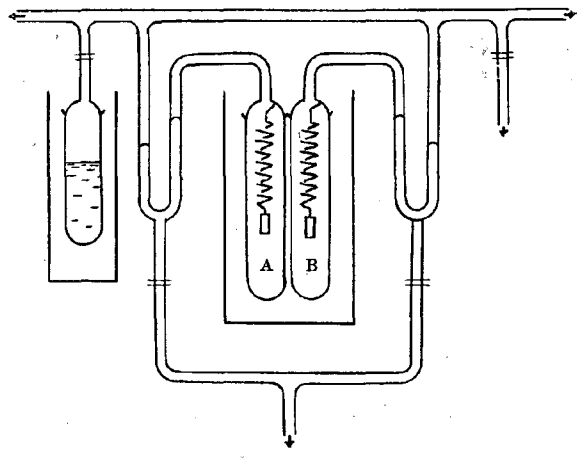


Fig. 4.4.

tric heating from the moisture-saturated state to the air-dried state and of the wood spontaneously dried were shown in Fig. 4.3. The experimental material was Japanese cypress plates with a dimension of 1.5 mm in fiber direction, 8 mm in tangential direction, and 100 mm in radial direction. The dielectric heating was performed at 100-105°C for three hours. The apparatus was the one previously described with a modification that, as shown in Fig. 4.4, a device was made to operate A and B synchronically by controlling mercury level for the purpose to achieve synchronicity of start of the water sorption.

The water sorption process under keeping vapor pressure at 7.2 mmHg is shown in Fig. 4.3 (a), and that under gradually varying temperature and vapor pressure in Fig. 4.3 (b). In both, the changes are quite similar below moisture content about 11 %, but along with increasing the moisture content the difference becomes distinct to reach a maximum difference at maximum equilibrium. This means that the constant c and ϕ_0 in the adsorption equation (3.21) do not vary but the constant n changes. In dielectrically heated wood, the value of n is small.

In deriving the adsorption equation (3.21), a model has been used, in which vicinal fibrous molecules present in the noncrystalline region increases the distance between them to form monomolecular adsorption layer when water molecules are adsorbed on the adsorption site in wood substance expect in very high pressure region. This is shown diagramatically in Fig. 4.5 (a) where

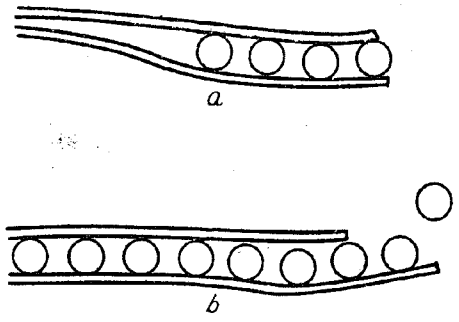


Fig. 4.5.

molecules are present in lines by monomolecular layer adsorption between the crystalline region and vacant vacuole in the space formed by two fibrous molecules. When $x \rightarrow 1$, the maximum value of water molecules in single line determines the value of n. Therefore $n \rightarrow \infty$ means, as shown in Fig. 4.5 (b), breaking of the linkage between infinitely long fibrous molecules or infinite swelling. When the length of the fibrous molecules is shorter, it is reasonably understood that a relatively small, definite value of n will cause infinite swelling. As exemplified in the above experiments, the increase of the value of n with no variation of other constants in the adsorption equation (3.21) means augmentation of the noncrystalline region and the decrease implies the augmentation of the crystalline region

On the constant ϕ_0.

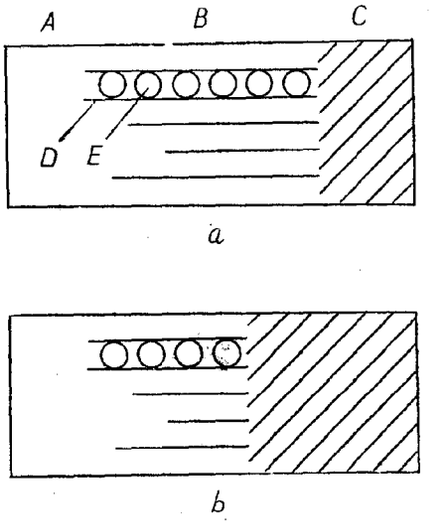


Fig. 4.6.

A : Pore. B : Amorphous region.
C : Crystal region. D : Wood substance molecule.
E : Water molecule.

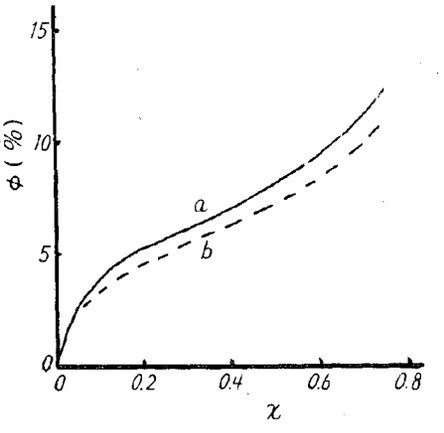


Fig. 4.7.

a : untreated.
b : treated.

Fig. 4.7 shows the results of the comparison of heat-treated dried wood and spontaneously dried wood. The sample is Japanese cypress. The heat-treatment was performed, after evacuation of the sample in a desiccator over phosphorus pentaoxide for approximately 4 hours and closing the cock, by placing the vessel in a thermostat at 130°C for 5 hours. The dimension of the sample plate and the apparatus for experiments are the same as used before. Isotherm were obtained at 25°C in thermostat. The values of the constants ϕ_0 and c, as obtained from the results, have revealed decrease of ϕ_0 and increase of c by the heat treatment as shown in Fig. 4.8. The increase of c would be due to the increase of the heat of adsorption in previous discussion.

The cause of the decrease of ϕ_0 may be either (1) variation in the crystalline region and (2) change in the constituents.

(1) Augmentation of the crystalline region : On an assumption that the constituents do not change, the mechanism of the decrease of ϕ_0 will be considered. Assuming $K_1=1$, the decrease of ϕ_0 will mean disappearance of some of the water molecules present on the position of $n=1$ in Fig. 4.5 (a). This is possible by the formation of strong linkage among some points of side chains (Stamm has suggested that this linkage is ether linkage[1] due to shortening of

[1] Stamm, A. J. & Hansen, L. A. : *Ing. Eng. Chem.* **29**, 831 (1937).

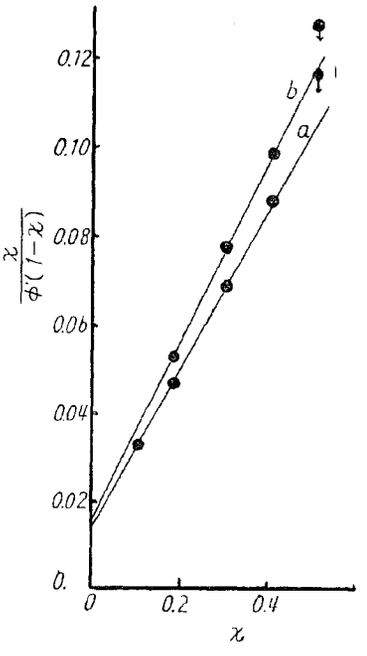


Fig. 4.8.

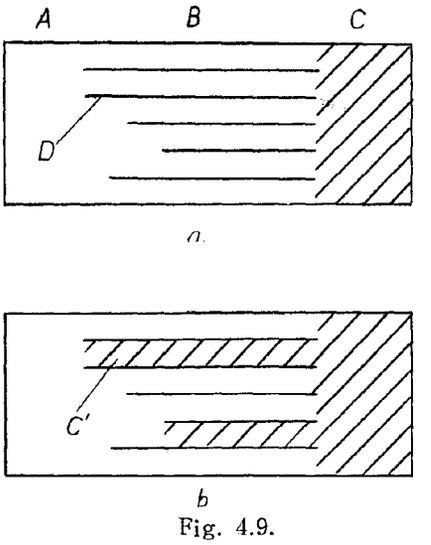


Fig. 4.9.

the interatomic distances during the two vicinal fibrous molecules running through non-crystalline region being activated for more vigorous Brownian movement by acquirement of heat energy, and so approaching and colliding water molecules can difficultly do Brownian movement and difficultly form the activated complex which makes the moisture adsorption process toward the right direction in the scheme :

$$\circ + \perp \rightleftarrows \varphi$$

$\circ$: water molecule

$\perp$: adsorption point

This is shown diagramatically in Fig. 4.9 (a) for untreated wood and in Fig. 4.9 (b) for the treated wood in which extruding crystalline regions, covered by oblique lines, is formed. There are therefore two mechanisms for the augmentation of the crystalline region, one is caused by the "n" effect and similar to the growth of glacial sugar. and the other is by the "ϕ_0" effect on the above assumption and falls in the same category as horn formation of Kompeito (confetto). The values of ϕ_0 obtained by the B. E. T. theory on the moisture adsorption in cotton and viscose rayon are 3% and 6%, respectively ; the amounts of crystalline region are 70% and 40%, respectively, according to Hermans[1].

[1] Hermans, P. H. : *loc. cit.*

(2) Change in the constituents : It has been reported that treatment of Sitka spruce at 135°C for 2 days produces the following changes (Hawley and Wiertelak[1]).

Constituents	Untreated wood	Treated wood
Reduction in amount due to decomposition	—	1.6
Lignin	28.5	33.6
Cellulose	56.8	51.0
Pentosan	7.0	4.7

Under the conditions of evacuation and low treating temperature and with very short treating period, the changes in the constituents of the sample plates in the present experimental system does not appear so large, if any. The moisture adsorbing ability of hemicellulose will be discussed in the next section.

4.4. Water Sorption of Hemicellulose

Hardwood consists of cellulose 50%, xylan 15-25%, lignin 25%, and others, while soft wood cellulose 50%, xylan 6-10%, mannan 5-10%, and lignin 30%. Of these constituents, cellulose and xylan have relatively similar chemical

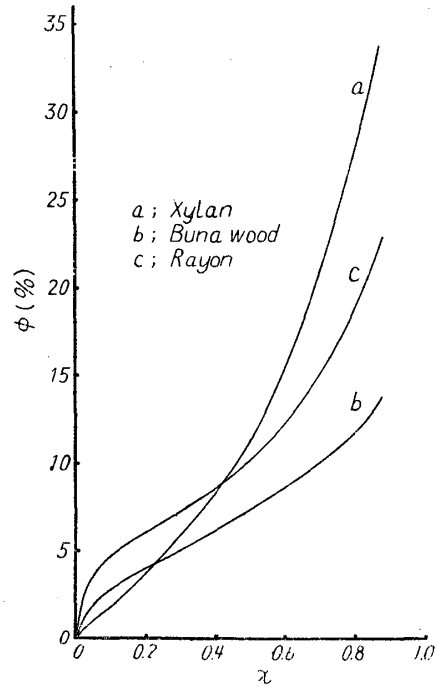


Fig. 4.10.

[1] Shibamoto, T. & Kuriyama, A. : Wood Carbonization (in Japanese) Tokyo, Asakura, (1952).

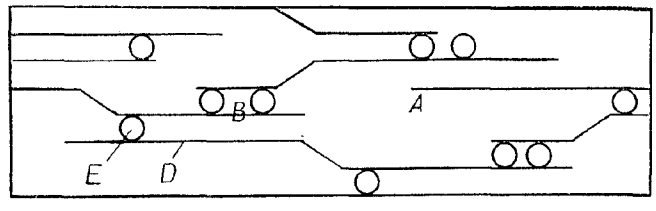
structures, but in contrast to the former which is long-chain molecule the latter has short-chain shape and lacks the reactive hydroxyl grouping on the sixth carbon of the unit sugar. The moisture sorption of xylan whose surface structure is now thus understood will be estimated and analysed by the author's equation.

The results of estimation of the isotherm on xylan, cellulose, and buna wood by the previously mentioned apparatus are given in Fig. 4.10. The xylan was prepared by extracting holocellulose of buna with 5% aqueous potassium hydroxide solution and drying from aqueous solution to a film. The sample of cellulose was untreated viscose rayon. From the data and equation (3.12) the constants are obtained as follows :

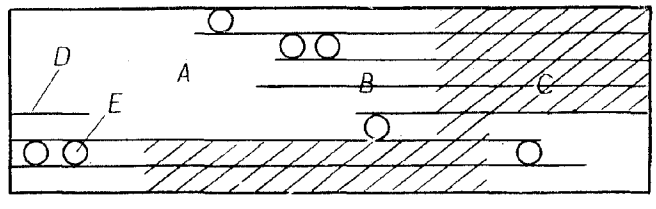
	c	ϕ_0	n
Xylan	0.9	19.6	5.1
Rayon	28.9	5.7	4.9
Buna wood	14.2	4.4	4.0

The difference in ϕ_0 between xylan and wood will be now considered.

Xylan has smaller degree of polymerization than cellulose, and so little crystallinity that the molecules are relatively less oriented. Consequently the internal surface of the primary layer at dried state in xylan is larger than that in cellulose. The value of $n\phi_0$ in xylan is 100 and calculation of the area of



a



b

Fig. 4.11.

A : Pore. B : Amorphous region. C : Crystal region.
D : Substance molecule. E : Water molecule.

the internal surface from this value gives 3500 m^2/g. Considering that xylan dissolves in water, this value means that it is equivalent to the area of whole surface of each melecule separated from each other. In addition, this implies that in little crystalline and short-chain molecules which have large ϕ_0 values, relativaly small n value causes infinite swelling (Fig. 4.11). Formerly the comparison between the crystallinity of rayon and wood was discussed. That will help to understand the difference in the ϕ_0 value in the above table.

It is also plausible that lack of highly reactive, hydrophilic groupings in xylan results in smaller adsorption energy and therefore smaller c value.

5. Conclusion

The studies heretofore described on the water sorption equilibrium of wood in narrow meaning with main emphasis on isotherm are summarized below.

The water sorption of wood is characterized by swelling owing to the existence of the non-crystalline region. The type of the water sorption can be classified into three types by the value of δv which is determined from the volume expanding coefficient (β) and specific gravity (γ_0) in the following formula :

$$\beta/\gamma_0 = 1+\delta v \tag{2.9}$$

The type I is the case where δv is larger than 0 and the volume expansion amount exceeds the volume of absorbed water, and it may also be called the balsa type. The type II shows a reversed feature and is represented by akagashi. The type III is a standard type where δv is equal to 0 and Japanese cypress is the representative of this type. Examination of thirty nine representative trees in regard to the relation of δv and γ_0 has revealed that along with larger γ_0, δv becomes smaller. Therefore, consideration on the mechanism of moisture sorption has been made on Japanese cypress which represents the standard type of moisture sorption of wood to point out that the water molecules approaching to the wood substance molecules by gas diffusion enter into combination with the latter under adequate conditions and augment the distances between vicinal fibrous molecules so as to make spaces in which the movements of other water molecules are possible. The enlargement of the distances elastically causes expansion of external dimension of wood and it has been found

that the amount of the change is equal to the volume of the bound water (Chapter 2).

From this finding, a model with expanding surface is presented by introducing ideas of the adsorption on the vacuole surface that would not contribute to the change in the external volume of wood and multimolecular layer adsorption. The following adsorption equation has been derived through dynamic consideration on this model.

$$\phi = \frac{c\phi_0 x}{1+cx}\left(1+K\frac{x-x^n}{1-x}\right) \tag{3.21}$$

This equation has well explained the data on moisture adsorption of wood in the whole range of $x > 0.05$, and the product of the constants n and ϕ_0 gives, as expected, approximate value of fiber saturation point. Examination of the constant K can suggest the amount of vacuoles and judge the presence or absence of multilayer adsorption. Furthermore, the constant c can give the heat of adsorption and the velocity constant. The constants in the above equation all can be obtained relatively easily and without the help of the trial and error method. The equation itself is simple and practical. It has additional excellency in covering the weak point of the B. E. T. theory which requires smaller moisture constant along with, curiously, raising temperature, and in covering the Hüttig's equation at an extreme case (Chapter 3).

Calculation of the area of the internal surface of dried wood from equation 3.21 on Japanese cypress gives about 230 $m^2/g.$, and the area expanded by moisture absorption up to saturation is about 700 $m^2/g.$ Examination of the adsorption heat distribution on these internal surface has shown that there are three kinds of surface : (1) the surface contributing to moisture absorption in the range of $x < 0.05$ and distributed exponentially, (2) E_1-surface, and (3) E_2-surface. In the next place, the constants obtained by analyzing the data of moisture absorption on heat-treated wood have been found to clarify the effect of heat-treatment on the fine strucutre of wood. It has also been demonstrated that the equation 3.21 can be applied to the moisture absorption of xylan membrane, a main constituent of wood and that there is a close relation with the molecular structure.

In conclusion, the adsorption equation 3.21 that is born on an idea of ex-

panding surface or swelling agrees well with estimated isotherms in wide region, and the constants determined from it are very significant in helping in elucidation of fine structure of wood.